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Vital Signs  
Long-Term Aquatic Monitoring Projects:

**Part C**

Draft  
Guidance on  
WRD Required and Other Field Parameter Measurements,  
General Monitoring Methods and Some Design Considerations in  
Preparation  
of  
A Detailed Study Plan

(Work In Progress)  
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## **PART C**

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## **6.0 References and Other Information Sources**

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## **7.0 Appendices**

- C-1 Book 9 – National Field Manual for the Collection of Water Quality Data (USGS) – Download at <http://water.usgs.gov/owq/FieldManual>
- C-2 Field Guide for Collecting and Processing Stream-Water Samples for the National Water Quality Assessment Program (USGS) – Download at <http://water.wr.usgs.gov/pnsp/pest.rep/sw-t.html>
- C-3 Guidelines and Standard Procedures for Continuous Water-Quality Monitors: Site Selection, Field Operation, Calibration, Record Computation, and Reporting (USGS) – Download at <http://pubs.water.usgs.gov/wri004252>
- C-4 State-by-State Look at CWA with Protocol Guidance and Multiple Sources of Water Quality Monitoring Information – Download at: [http://www.rivernetwork.org/cleanwater/cwa\\_search.asp](http://www.rivernetwork.org/cleanwater/cwa_search.asp)
- C-5 Example Field Forms, Calibration Forms/Worksheets and Instrument/Vendor-Specific Calibration Tips (see also <http://www.tnrcc.state.tx.us/admin/topdoc/gi/252/swqmproc.pdf>)
- C-6 Water Quality (Monitoring) Information System Design Framework (from Ward, 1998)

## ACRONYM LIST

ANC	Acid Neutralization Capacity
APHA	American Public Health Association (Std. Methods)
BOD	Biochemical Oxygen Demand
°C	Degrees Centigrade or Celsius
CAFO	Confined Animal Feeding Operation
CCC	Chronic Concentration Criteria
CERCLA	Comprehensive Environmental Response Compensation & Liability Act
CLP	Contract Laboratory Program
CWA	Clean Water Act
DO	Dissolved Oxygen
DOE	Department of Energy
DOI	Department of Interior
DOT	Department of Transportation
DQOs	Data Quality Objectives
EDI	Equal Discharge Increment
EPA	Environmental Protection Agency
EWI	Equal Width Increment
GPRA	Government Performance and Results Act
GIS	Geographic Information System
HIF	Hydrologic Instrumentation Facility
HPLC	High Performance Liquid Chromatography
IPT	Inflection Point Titration
ISE	Ion-Specific Electrode
JHA	Job Hazard Analysis
LED	Light Emission Diode
MV	Millivolts
NAWQA	National Water Quality Assessment
NELAC	National Environmental Lab Accreditation
NFM	National Field Manual

NFM#	National Field Manual (Book #)
NIST	National Institute of Standards and Testing
NPDES	National Point Discharge Elimination System
NPS	National Park Service
NRC	Natural Resource Challenge
NTU	Nephelometric Turbidity Unit
NWIS	National Water Information System
OD	Outer Diameter
ORP/Eh	Oxidation-Reduction Potential
ONRWs	Outstanding Natural Resource Waters
OSHA	Occupational Safety and Health Administration
PAR	Photosynthetically Active Radiation
POPs	Persistent Organic Pollutants
POTW	Publicly Owned Treatment Work
PPE	Personal Protective Equipment
PVC	Polyvinyl Chloride
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
SC	Specific Conductance
SOPs	Standard Operating Procedures
STORET	Storage and Retrieval
TDS	Total Dissolved Solids
TGP	Total Dissolved Gas Pressure
TMDL	Total Maximum Daily Load
USDA	United States Department of Agriculture
USGS	United States Geological Survey
WRD	Water Resources Division
WSP	Water Supply Paper
WTP	Wastewater Treatment Plant
YSI	Yellow Springs Instruments

## DRAFT

## PART C

## 1.0 Scope of this Guidance on Field Measurements

## 1.1 Introduction:

The focus of this guidance on water quality field measurements is to provide a Servicewide basis for obtaining a consistent, representative, and comparable field data set that the Park Service can utilize to evaluate primarily surface water quality over the long term. Surface waters ranging from “impaired” based on a State-designated beneficial use, to those designated as pristine or Outstanding Natural Resource Waters (ONRWs) (by States or others) are of primary concern. This guidance seeks consistency with the vision and objectives of the Natural Resource Challenge, focusing more in the area of what to do in the field to ensure data collected is representative and collected in as consistent a way as possible between Networks. Water Resources Division has presented strategies for Parks to use in designing and implementing simple, cost-effective, surveys and monitoring of water quality impacts from various land uses and activities in and around National Park Service units (Kunkle et al, 1987). That document is an excellent primer for relating common sources and impacts of pollution to the more diagnostic monitoring parameters. The Vital Signs Program now offers the opportunity to further develop and implement with greater consistency those monitoring strategies over the long term and on a national scale.

Part C of this guidance does not provide or describe detailed step-by-step instructions on how to perform field measurements (field protocols) beyond that produced by others and recommended here (provided in various appendices, references etc.) or recommended protocol sources (e.g. authorized States under Clean Water Act). There are simply too many site, instrument, and sampling variables in addition to locally driven variations in sampling objectives, to produce a single protocol that can be applied universally across all Networks covering all situations. Therefore, the protocols of an established program (National Water Quality Assessment Program, NAWQA) having national scope and a proven track record are recommended in this Guidance as a **default protocol** (standard) with various **State protocols for water quality monitoring a preferred option where a regulatory issue under the Clean Water Act (CWA) establishes a governing criteria or standard**. An excellent, comprehensive **example of an updated State field procedures guidance (August, 2003) for marine and freshwater aquatic environments that many Networks may choose to review and use (in conjunction with guidance from pertinent states in their Network) may be found at: <http://www.tnrcc.state.tx.us/admin/topdoc/gi/252/swqmproc.pdf>**. This or other comparable state field procedures guidance should be useful in preparation of the Network’s detailed water quality monitoring plan.

The best approach for Networks to ensure that field measurements are most representative is to ensure that field personnel (in-house staff, cooperatives, or

contractors) are well trained, that they have gained some level of experience through apprenticeship, that field technicians exhibit a professional's attention to detail, that equipment calibrations are well documented and performed carefully and consistently following manufactures instructions, and that protocol development has followed the "planning process steps" outlined in Part B of this guidance document.

This field guidance for monitoring surface water is not intended to be a stand alone document or exhaustive compilation of the various field methods used in water quality sampling and monitoring. Nor is the intent to duplicate some excellent guidance that has been developed previously by other Federal Agencies such as the USGS in its implementation of the NAWQA Program or EPA through its EMAP program or that of various State agencies. Rather, the goal of this document is to provide Networks general guidance in several areas from a WRD perspective as manager of the data set and charged with a responsibility to facilitate implementation of a successful Servicewide water-quality monitoring program. The Water Resources Division (WRD) will make recommendations where from it's perspective, a particular course of action will be or has a greater likelihood of being compatible with the goals expressed in the Natural Resource Challenge (NRC) Vital Signs program and meeting the National Park Service (NPS) five year strategic plan and goals of the Government Performance and Results Act (GPRA). GPRA goals that stress measurable and quantifiable results are the primary directive for water quality monitoring under the Vital Signs program. Numeric criteria and narrative standards of the CWA offer a means to assess or quantify water quality.

WRD views the overall water quality monitoring component of the Vital Signs program as generally consisting of three (3) steps or activities organized at the Network level. These steps include:

1. Planning and Assessment (Step I)
2. Design (Step II)
3. Implementation (Step III)

Each step will include multiple components that will ultimately produce a **water quality information (monitoring) system (Ward, 1998)** for each Network that Parks will use in their management of their aquatic resources. For example, the Planning and Assessment Step (I) would likely include a Network-wide identification and assessment of key stressors to the water quality of significant water resources to the Network's Parks (e.g. point and non-point sources, air deposition contaminant concerns etc.), a survey of Park water quality issues (by questionnaire and follow-up meetings), retrieval of historical water quality data and evaluation of existing public data bases (e.g. EPA's Storage and Retrieval (STORET) water quality database, the USGS National Water Information System (NWIS), and National Park Service individual park reports (Baseline Water Quality Data Inventory and Analysis reports, Level I Inventory reports etc.), review of previous scientific research at Parks dealing with water quality, retrospective analysis of previous water quality monitoring in and around Network Parks, development of various GIS data bases and mapping themes (e.g. land use), identification and location of past and current monitoring activities (sampling locations and analytes) by potential



cooperative agencies (federal, state, and local), and the location of gaging stations for sources of flow/discharge information etc..

An important product of the Phase I effort would likely be a geographically referenced Network Geographic Information System (GIS) database consisting of several themes or layers of information useful to developing a monitoring system. Network-wide or more local maps at various scales could then be produced showing Park locations, their boundaries and their significant water bodies; political/regulatory boundaries (e.g. States); watershed boundaries; various major point dischargers (NPDES); types of land use; existing monitoring and gaging stations; nearby sites on EPA's Comprehensive Environmental Response Compensation and Liability Act list (CERCLIST) etc.; to mention only a few possible elements of a GIS database.

This and other information would then be available for the **design of the water quality information system or monitoring program**, so that a **common vision** of what a water quality monitoring system should look like might be developed for the Network Board of Directors and other participants in the program. Ward (1999) summarizes five (5) critical steps in the design of a water quality information system. These system design components are reproduced in Appendix C-6 for Network consideration in their design efforts. The actual monitoring network design component and data collection procedures (steps 3 and 4 of Ward) would largely address, the who (staffing; in-house, cooperators, contractors etc.) of performing the actual sampling and analysis (laboratory), the what (field and laboratory measurements to collect at each monitoring station), the when (the sampling frequency appropriate at each monitoring station), the where (location of monitoring stations), and after presumably several iterations, arrive at a program cost that matches the Network funding available in conjunction with any support of cooperative agencies. A weakness of monitoring programs is that a few individuals often make these design decisions on an ad hoc basis without the design decisions being well documented or a purpose of the monitoring made clear. This can result in considerable data being collected without a means of converting it to useful information that can be used by resource managers. Another weakness is the selection of measurement parameters to be used for trend analysis without an **understanding of the natural variability** (see Part B for discussion of this issue).

This guidance is written with the underlying assumption that each one of the three steps (above) could take up to a year for Networks to complete with implementation of the first year of water quality monitoring occurring at some point in the 3<sup>rd</sup> year (pilot monitoring) or 4<sup>th</sup> year (full implementation) of the Networks water quality funding. Water Resources Division has fully adopted the concept of integrating design and implementation of water quality monitoring with the network-based Vital Signs monitoring program (**incorporate 3-phased approach to monitoring plan development and same implementation schedule**) developed by the Natural Resources Information Division (see May 2002 memo from Associate Director to Regional Directors). A **detailed water-quality monitoring plan** would be submitted to WRD for approval at completion of Phase III of monitoring plan development and prior to implementation of the Networks overall water quality monitoring.

General topics/areas that are addressed to varying degrees in Part C include:

- 1) Data requirements and data quality WRD sees as a necessary component of a long term water quality monitoring under the NRC/Vital Signs program, that will meet the data representativeness, consistency, and comparability goals of a Servicewide program, including the various methods of water quality monitoring that have a track record of producing acceptable data sets to support evaluation of ONRWs, impaired waters, and trend analysis over the long term
- 2) Generally accepted guidance on water quality monitoring and protocols that are available as a resource to be used by Networks in development of their detailed water quality monitoring plan and general monitoring information to be considered under the Natural Resource Challenge Vital Signs program for a variety of conditions (streams, rivers, lakes, wetlands, and the marine/estuarine environment)
- 3) Technological developments that have occurred in water quality monitoring and the new instrumentation that is developing to support both intermittent (synoptic) and continuous monitoring of field measured parameters
- 4) WRD's effort to establish a basic or "core" set of minimum required water quality parameters for freshwater and marine/estuarine environments. These parameters would be collected Servicewide at all monitoring stations to establish baseline conditions for impaired waters and Outstanding Natural Resource Waters (ONRWs). Rationale for their selection and discussion of their utility is also provided.
- 5) Aspects of data base maintenance, what will be available and how it will be used, availability of historic data, documentation of collected data and how it will be stored, retrieved and archived to meet the program goal (see also Part E)
- 6) An expanded listing and discussion of some of the more important but optional field parameters beyond the basic set, that should be collected at the discretion of individual Networks to meet Network/Park specific water quality monitoring needs and objectives and to include some discussion of why, where, and when it may be most appropriate to include these parameters in a Network monitoring program

In general, this guidance follows and relies heavily upon field protocols developed under the NAWQA program by the USGS. NPS Network staff, cooperators, and contractor's are referred to **USGS Book 9 of National Field Manual (NFM, 1998)** and the **Field Guide for Collecting and Processing Stream-Water Samples for the National Water-Quality Assessment Program (Shelton, 1994)**, to supplement this guidance and provide a more comprehensive and in depth presentation and discussion of field methods that could not be undertaken here (see Appendix C-1). It is assumed Networks will review and incorporate procedures guidance from States in their Network in developing the detailed monitoring plan. An excellent example of State water sampling procedures guidance that Networks may find very useful is recommended for review prior to detailed monitoring plan development. This document (see <http://tnrcc.state.tx.us/admin/topdoc/gi/252/swqmproc.pdf>), plus procedures guidance (where available) from States within the Network will be key in understanding the subject matter to be discussed and referenced in the detailed monitoring plan so that WRD may determine if the proposed implementation of the monitoring program is viable. Also, EPA's Ecological Monitoring and Assessment Program (EMAP) has developed protocols for freshwater and marine/estuarine monitoring that may be adopted by Networks in instances where data quality objectives are compatible.

In some cases, where a Network's more **significant surface water bodies** are already well-monitored under current programs, a Network may determine that some small portion of water quality program funding should be devoted to groundwater monitoring. However, the conclusion that a Network's major surface water bodies are adequately monitored, should not be reached by a Network without significant supporting documentation that monitoring of significant surface waters includes both the required "core" parameters and Park/Network stressor or issue-based supplemental parameters. Furthermore, the Networks should establish that such monitoring of major water resources by Parks or by other entities is likely to continue over the long term to support the Servicewide GPRA goals. Generally, alternate funding programs should be identified for monitoring of groundwater resources that may be impacted by more localized contaminant releases.

The complexity of implementing a water quality monitoring program Servicewide that necessarily deals with a vast variety of water body types, site-specific conditions, and **varying regulatory context (by State) that can drive the protocol used, precludes WRD from generating a single comprehensive protocol that addresses all situations adequately or appropriately.** National programs conducted by the United States Geological Survey (USGS) such as the National Water Quality Assessment program (NAWQA) and EPA's EMAP program have generated detailed guidance and protocols for sampling both surface water and ground water. In addition, guidelines have been recently published by the USGS for continuous water-quality monitors that may be applicable to Networks interested in state-of-the-art monitoring methods providing the most temporally complete data sets for basic water quality parameters at their more significant natural resource waters.

The USGS Hydrologic Information Facility (HIF) (<http://www.hif.er.usgs.gov/uo>) has also tested a wide variety of equipment used in water quality monitoring and general hydrologic data gathering to support various research of the USGS. Several sources of information have been utilized extensively in preparing this guidance. The major sources such as the USGS NAWQA protocols can be found on the web (<http://water.usgs.gov/owq/Field Manual/>) and should be downloaded and included as Appendix C-1 to this document. Inclusion of this document as an appendix was done to facilitate ready access to information deemed critical to understanding this guidance and to highlight WRD's default protocol selection for field execution. In addition, several web sites are referenced throughout this document to reflect other important supplemental information/resources.

Most States have also developed water quality monitoring protocols to support their establishment of lists of impaired water bodies within their jurisdiction (303d lists), aid in the identification of outstanding natural resource waters, facilitate implementation of permits under the National Point Discharge Elimination System (NPDES) program, and initiate the development of Total Maximum Daily Load (TMDL) studies. Where appropriate, such as **monitoring state listed impaired water bodies or in some other regulatory context, Network staff should consult monitoring protocols of individual States for primary guidance** to determine if some variation of protocols generally recommended here (largely those of the USGS NAWQA program) should be modified. An excellent resource for a state-by-state breakdown of the actual standards and criteria (NPDES, TMDL, and Biologic Monitoring) promulgated by States (authorized) under the Clean Water Act may be found at [www.rivernetwork.org/cleanwater/cwa\\_search.asp](http://www.rivernetwork.org/cleanwater/cwa_search.asp).

A protocol (Step VI of the overall planning process outlined in Part B of this document at <http://science.nature.nps.gov/im/monitor/protocols/wqPartB.doc>) consists of (1) **a narrative** and (2) **Standard Operating Procedures (SOPs)** that are written for and often times in part by the people actually doing the work (Oakley and Boudreau, 2000). Due to the variables mentioned above that can dictate or influence the protocols followed, WRD views water quality monitoring protocol development as a Network-specific document that can sometimes vary on a monitoring site-specific basis in response to meeting a particular state's regulatory or monitoring requirement or standard. Thus, an acceptable protocol to provide a basis for de-listing a 303d listed water body or establish an Outstanding Natural Resource Water (ONRW) in one state may not be an acceptable protocol to follow in an adjoining state. Networks crossing state boundaries (as nearly all do) need to be cognizant of this in their protocol development. Only protocol development at the local level is likely to avoid such potential for error. Oakley and Boudreau (2000) lay out the key features of protocols and provide general guidance on protocol development. More detailed protocol development considerations are discussed in Part B of this guidance.

Groundwater monitoring is not a part of this guidance and groundwater-monitoring protocols are not addressed here. The Networks are directed to the NFM, EPA, and States for guidance and more specific sampling protocols that address groundwater monitoring should that be a component of their overall program. Review of

applicable state, federal agency, and other protocols deemed appropriate to meet water quality monitoring objectives of the Network and those set forth in this guidance to meet Servicewide goals are all strongly encouraged.

The Networks should develop a detailed water quality monitoring plan specifying the major/most significant water bodies identified in the Network, location of the monitoring stations to be established, the parameters to be measured at each station with the data objectives of that monitoring, the sampling protocols to be followed (may vary by state), the quality assurance and quality control measures and any statistical analysis of the data that will be undertaken (see Part B for more detail). Ideally, much of the basic information could be provided in map form showing the Network area, Park, watershed, and other political (state) boundaries, monitoring station locations and locations of key stressors to water quality that currently impact Parks or may in the future (development areas, major waste outfalls/POTWs, general land uses that can degrade water quality etc.).

## 1.2 General Guidance for Data Collection

The field technicians responsible for collecting water quality data under the Vital Signs Program should not proceed without consulting the USGS National Field Manual (NFM) upon which much of this guidance is based. WRD recommends that these be the default protocols to generally follow. In addition, other appropriate state and federal agency guidance should be sought that may be locally applicable to surface water monitoring requirements due to specific 303d list impairments or other regulatory considerations. In general, **water quality monitoring using sampling and analysis methods or field procedures that do not meet the standards of the authorized or governing regulatory body should be avoided.** Technical guidance produced by the appropriate vendors or manufacturers of field equipment must necessarily be consulted as well, particularly in the realm of specific equipment operation and maintenance. [Note: any mention of manufacturers and product names does not constitute endorsement by the federal government]. If continuous monitoring is anticipated for one or more stations or use of multiparameter equipment (recommended) is planned, then the **Guidelines and Standard Procedures for Continuous Water-Quality Monitors, Site Selection, Field Operation, Calibration, Record Computation, and Reporting (Water-Resource Investigation Report 00-4252 of USGS)** is a highly recommended source. This document should be downloaded and added as Appendix C-3 by accessing the web at <http://water.usgs.gov/pubs/wri/wri004252/>.

All water quality personnel collecting data should have had formal training and some period of field apprenticeship in order to correctly calibrate and operate field equipment, implement sampling procedures, and document the field protocols used and sampling results with the necessary metadata. The Networks may choose to initiate monitoring with Network/Park staff or transition water quality monitoring responsibilities from contractors/cooperators or USGS personnel to permanent Network staff as the program evolves. Training and apprenticeship for Park Service technicians should be planned and budgeted prior to execution of monitoring activities by NPS staff. The

USGS regularly offers a course entitled “**Field Water Quality Methods for Groundwater and Surface Water**” held at the USGS National Training Center in Denver, Colorado. NPS staff and cooperators may attend on a space available basis. Stednick (1991) is also a good resource in its discussion and review of basic chemical relationships and solution chemistry concepts related to conducting water quality monitoring and its broad overview of water sample collection procedures, field measurements and basic statistical concepts.

Field training is necessary to ensure field sampling tasks are performed safely, achieve the most representative measurements possible, and data is consistent and comparable Servicewide. It is recommended that each Network considering initiating Vital Signs long term water quality monitoring using Network staffing consider at a minimum, a full time water quality field sampling team of no less than one qualified, Network-based, lead technician and a commitment from Parks to supply one dedicated staffer when sampling at Parks. The lead technician should be co-located with a small lab central to the Network to facilitate timely access to Network monitoring stations and the support (dedicated vehicles, field instrument calibration, ordering of reagents and calibration solution preparation) necessary to conduct fieldwork. All Network staff involved in the water quality component of the Vital Signs Program and the sampling technicians in particular, should have a thorough understanding of the program objectives. Some level of coordination or cooperative effort with the local NAWQA/USGS water resources office and other federal/state/local water quality district offices and monitoring organizations should also prove highly beneficial and allow for maximum use of limited monitoring resources.

Networks that intend to perform water quality monitoring with in-house resources should establish the necessary support structure including budget, human resources, facilities, and equipment as well as understand the level of coordination that implementing successful water quality monitoring program will entail. A Network lab equipped with all necessary equipment, reagents, and calibration solutions should be established to support field sampling when undertaking a long term program of this magnitude. In order to answer some questions, a high frequency of station sampling may be required to provide definitive long-term results. Depending on the question to be answered, the frequency of sampling could be monthly or even more often. This will place significant demands on human resources. Budgeting and procurement of all necessary equipment needs to be planned well in advance and dedication of specific field vehicles equipped to perform water quality sampling and process samples in a clean environment that minimizes the potential for sample contamination is also very important.

## 2.0 Surface Water Types

Networks will identify a variety of surface water **types** (Freshwater and Marine/Estuarine water bodies) in their watersheds/coastal areas that are deemed significant or important candidates for long term monitoring. For Networks including

Parks with one or more marine/estuarine water bodies, bays, lagoons, and even open marine areas may be considered for long term monitoring. Factors affecting the selection of surface water monitoring points under fresh water, brackish water or marine conditions and the associated sampling methods employed, fall into two broad categories. 1) **Fast flowing water** is sometimes sufficiently well mixed with relatively uniform chemistry so that a single sample (e.g. at the stream centroid) may be representative. 2) **Still water** chemistry is subject to potentially greater spatial variation or vertical gradients and may require some spatial and/or vertical integration of field parameter measurements, or sampling of multiple sites for adequate spatial characterization of the water body. Anticipating how a particular water body may vary in key parameters (both spatially and vertically) and the questions to be answered by that monitoring is critical in selecting the appropriate monitoring method and system design.

## 2.1 Still Water

For slowly moving or still water (streams, rivers, lakes, ponds, estuaries, bays), multiple points of measurement may be needed to obtain a representative set of field measurement values that best describe the water quality parameters. In stream monitoring, several sets of field measurements made at discrete depths taken along a stream cross section are recommended. All the individual parameter data collected in this manner should then be recorded and the mean selected to provide the most representative measurement of that particular parameter (i.e. do not average each set of parameters measured in the vertical first but treat each measurement as a station/sampling point for averaging). Note that to average pH measurements, the pH values must first be converted to the antilog, an average value computed, and then converted back to the log value when a mean value is computed. In some instances a median pH value is appropriate but this should always be documented in the metadata.

Still-water sites refer to lakes, reservoirs, ponds, swamps, marshes, riverine backwaters or any other water body of various size or shape where water generally does not move unidirectionally (NFM 9). In monitoring still or standing water, it is beyond the scope of any monitoring program to sample for every condition that can be found in these water bodies. Therefore, deciding what specific condition is being targeted (if any) and where to focus sampling efforts based on the sampling objectives should be paramount. Standing water bodies often develop a physical-chemical stratification in their parameter values and although spatial water quality information may be cost prohibitive to obtain due to the number of monitoring stations required, representative information of the vertical stratification of the water body at a single location may be readily collected and can be generally representative of the water body condition. Parameter data in the vertical dimension is often representative of a larger area beyond that of the monitoring point. Such water quality profiling of standing water bodies is required under this program. Continuous monitoring stations, equipped with multiparameter probes deployed on buoys that are automated and timed to raise and lower the sondes at specified intervals, are sometimes used to perform profiling of standing water bodies in long term deployments. Selected laboratory parameters when

coupled with field measurements collected in this manner can be an important data set in understanding eutrophication of a water body.

## **2.2 Flowing Water**

Streams and rivers (fast or slow, intermittent, ephemeral, or perennial), canals, ditches, and flumes of all sizes and shapes or any other surface feature where water moves unidirectional (including parts of reservoirs and estuaries, and some marine water bodies dominated by strong currents) are considered flowing water sites (NFM 9). Under flowing water conditions such as those found in a stream or river, a single set of field measurement data collected along a stream's cross section is used to represent the entire stream at that point. To obtain data representative of the section, the variability of discharge and field parameter measurements across the stream must be known. The USGS uses this information to determine if equal discharge increment (EDI) or equal width increment (EWI) methods are most applicable. If the discharge is known the EDI method can be used. If the discharge is not known, the EWI method is used.

As a rule of thumb, a stream (riffle area) should be divided into a minimum of ten (10) increments/verticals and numbers of increments should increase with less apparent mixing of a stream. Knowledge of stream flow distribution in cross section is necessary to select verticals at which measurements will be made and/or sub samples collected. At a minimum, a stream should be characterized by such sampling at times of peak flow and base flow to establish that the stream is in fact, well mixed. A well-mixed stream should not vary in parameter measurements by more than the stabilization criteria listed in Table C-1. Once it has been established that the flowing body of water is well mixed, a single sample collection point from the midpoint of the stream at mid-depth (or at any convenient point in the stream) is generally sufficient for future sampling purposes. The reader is directed to Chapters A1 of the NFM field protocols for guidance in sampling site selection and to Chapter A6 for an expanded discussion of how and when to employ discharge weighted parameter methods (Appendix C-1). The flow chart (Figure 6.0-1) provided in the NFM shows the steps taken for in-situ measurement procedures for surface water.

## **3.0 Safety Issues**

Safety of field personnel should always be the first concern in conducting a sampling program and in the selection of sampling sites. Numerous safety issues and concerns are associated with implementing a long-term, Servicewide, water-quality monitoring program that includes extensive fieldwork and sampling by Network staff or other cooperators/contractors. The desired sampling frequency for most monitoring, necessitates exposure of sampling technicians to a variety of potentially hazardous field conditions across all seasons and climatic conditions in addition to unforeseen,



potentially catastrophic, short-term natural events (e.g. floods, storms) that may occur during the field effort.

As a result, field sampling requires planning that anticipates the risks and dangers that field personnel may be exposed to so precautions may be taken to limit threats to human safety as much as possible. For a program of this magnitude and duration, Networks should consider preparation of and operation under a health and safety plan along the lines of those developed for work at Comprehensive Environmental Response Compensation and Liability Act (CERCLA) sites or the USGS equivalent of a job hazard analysis (JHA). Such plans typically identify the general hazards for sampling staff to be cognizant of and hazards that may be unique to particular monitoring stations within the Network. In addition, nearest hospital facilities to each sampling site, the most direct route from various sampling sites to the hospital and emergency phone numbers are typically documented in advance. Applicable elements for a Network-specific water quality monitoring safety plan that address physical hazards common around water and biological hazards, largely due to poisonous plants and animals are also documented. A thorough review and familiarity with the safety plan should be required of all sampling personnel and a copy of the plan for ready reference should always accompany sample technicians to the field.

Network staff are referred to Chapter A9 of the USGS NFM for information about hazards water quality monitoring field personnel may encounter during field work and the procedures that, when implemented properly, will help ensure their safety and health. Topics addressed in this document include general references for federal policies and Department of Interior (DOI) safety guidelines; safety policies you are required to know and follow under the Occupational Safety and Health Act (OSHA), Environmental Protection Agency (EPA), and Department of Transportation (DOT); understanding and implementing a job hazard analysis (JHA); requirements related to use of personal protective equipment (PPE) on the job; safety training and certification requirements; safety issues associated with transportation and operation of vehicles (road vehicles and trailers, watercraft, aircraft etc.) used to reach sampling sites; surface water activities (e.g. wading, working from bridges, boats and cableways etc.); working around machinery, pumps and other equipment; working with chemicals, their proper use, handling, transport, storage, and disposal; handling of contaminated water and limiting exposure to yourself and others; environmental conditions caused by extremes in temperature (hypo & hyperthermia), sun exposure, and precautions taken to avoid threats posed by thunderstorms, tornados, hurricanes, floods, earthquakes, fire, snow, ice, and various animals and plants. Helpful checklists for standard safety equipment, for vehicles and vehicular laboratories, and for watercraft provide important items for reference. WRD anticipates that Networks performing any monitoring activities in-house will adopt this or some similar safety plan guidance under which all field activities should be governed.

#### **4.0 Monitoring Network Design Considerations**

This guidance divides fixed station water quality monitoring (e.g. the 4 required basic/core water column parameters and other sensor-based parameter measurements) into two categories. They are 1) **continuous monitoring** which is largely an automated parameter measurement and recording system with measurements made typically at short intervals and 2) **discontinuous/intermittent monitoring (synoptic)** which is more of a manual measurement process involving repeated monitoring station visits at some regular but longer-spaced measurement interval to collect data. Networks should **be sure to specify the type monitoring to be performed at each monitoring station, the equipment planned for use in collecting field measurements, the parameters intended for lab analysis, and the protocols they intend to follow in the detailed monitoring plan submitted to WRD.**

Intermittent monitoring often includes additional/concurrent sampling for off-site lab analyses. Continuous monitoring is characterized by in-situ probe measurements with time intervals between repeated measurements being sufficiently small (minutes to hours), that the resulting record of water quality can be considered continuous because few if any significant water quality changes are likely to go unrecorded. Discontinuous/intermittent monitoring is characterized by a time interval between repeated measurements at a fixed station sufficiently long (several days, weeks, months, or more), that one or more changes in water quality of the water body (e.g. diurnal fluctuations or those associated with a hydrologic event) are likely to have occurred that may not be reflected in the data.

Continuous monitoring (of core parameters) is sometimes necessary to answer certain questions, especially if the variable of interest has a high daily or seasonal variability. Continuous monitoring provides the most comprehensive temporal data set upon which to establish variability through time, an important issue when trying to document correlations, possible cause and affect relationships and differentiate natural variability from anthropogenic induced change to an aquatic system. When a data goal is to characterize events of short duration, but such events are difficult to capture manually, continuous monitoring is appropriate. It is recommended that if the Network identifies a significant water resource (water body) that exhibits events of short duration and high variability, continuous monitoring be considered. Data from continuous and discontinuous monitoring stations may then be generally compared to determine how sampling frequency may impact the range of observed parameter values.

Generally, for discontinuous sampling to approach the level of completeness of continuous sampling, water bodies must be sampled manually at very regular (short) intervals, (e.g. at the same time of day, and at multiple periods of the day when diurnal and other effects on various parameters are at their extremes). Other longer cycle maxima/minima (e.g. freeze/thaw, peak/low flow etc.) are also encountered in discontinuous sampling only rarely (usually fortuitously), despite their importance in understanding a water body's physical-chemical ebb and flow and in understanding the effects parameter changes have on aquatic organisms.

The advantage of continuous monitoring is the ability to recognize short-term changes (e.g. diurnal, precipitation related events etc.) or trends that would not be readily apparent or could complicate the understanding of long-term data in deciphering cause and effect. Analysis of continuously monitored basic parameter data may also be used to determine the best time(s) to collect other samples for lab analysis. Telemetry hookups that provide real time or near real time data also have the advantage of rapid recognition of an approaching peak flow event or problem sensor. Sampling may be initiated or a corrective action may then be taken before significant data is compromised or lost.

Because intermittent or discontinuous sampling is performed manually requiring multiple field mobilizations, the logistics problems and cost involved in shortening the intervals separating sampling events to that which monitors short term natural changes that are easily captured by automated continuous systems is impractical.

Continuous monitoring also allows better recognition and separation of the short-term variability effects when data is being evaluated for long-term trends. Given the developments in automated continuous monitoring over the last 5 years, it is likely that within the next 15 to 20 years, a higher percentage of water quality monitoring will become fully automated and continuous for at least the several basic water quality parameters.

#### **4.1 Continuous Monitoring**

Wagner and others (2001) indicate that four principal interrelated elements should be considered in the selection of a water quality monitoring system involving electronic data acquisition. They include (1) the purpose of the data collection (2) the type of installation (3) the type of sensor deployed at the installation and (4) the specific sensors needed to satisfy the accuracy and precision requirements of the data-quality objectives. These elements are critical to the design phase of any fixed-station monitoring program.

Continuous monitoring may be divided into two types on the basis of whether or not the data capture requires a manual component. A fully automated continuous monitoring station captures and records basic parameters automatically with a data logger built into the multiprobe system (datasonde). This data logger then either regularly downloads and transmits data via radio, telephone, or satellite to an offsite location (office) or provides the data to the offsite location continuously in real time. Some systems are now capable of providing real time information to a web page for viewing by the public.

In the absence of some form of telemetry (radio, satellite, telephone) hookup to an offsite location, continuous monitoring requires an onsite data logger or use of a datasonde that requires regular (weekly to monthly) site visitation by a technician and manual downloading of recorded data to a hand held data recorder or laptop computer. Alternatively, a data capture/data logger device may be located separate from the sonde, such as on the bank, and linked to the submersed sonde by cables.

Because current probe technology is limited more by instrument drift and probe fouling of different forms rather than data capture and record storage limitations in the datasonde, instrument deployment periods are generally limited to from one to a few weeks without requiring some form of probe maintenance. Maintenance intervals for deployed probes, primarily depends on a water's tendency to facilitate chemical precipitation or biological growth on the probes (probe fouling), how prone a particular probe/sensor's electronics is to drift, and the dependability of various mechanical systems (e.g. wiper blade for one or more sensors & shutter system of a turbidity probe). Under more favorable deployment conditions, some multiparameter instruments may not require servicing for a month or more and some new extended deployment systems (EDS) also fit pH and DO sensors with wipers to extend intervals between maintenance even further.

Three areas require the application of quality assurance/quality control (QA/QC) protocols when multi-parameter electronic instruments are used to collect water quality data. These include 1) sensor validation in the field; 2) time control for data loggers and 3) precision and accuracy of sensors over time (Whitfield and Wade, 1993). Stednick and Gilbert (1998) discuss briefly the field verification of multiprobe electronic data using independent sensors, performance of time checks of the data logger's internal clock recorder, and divergence of like sensors over time due to instrument drift. One means of dealing with quality assurance/quality control (QA/QC) issues with multiparameter measurements used in continuous monitoring situations is to use the initial measurements of a calibrated replacement sonde for comparison with the last measurements of the instrument being replaced or "swapped out". However, the USGS protocol calls for the use of standards/buffers, water baths, or calibrations under saturated conditions (dissolved oxygen/DO) both before and after sonde deployment (pre- and post-calibrations) to verify operation of the equipment and QA/QC.

Checking the in-situ deployed sonde against a recently calibrated multiprobe used to collect data manually is also a means of determining the correction for drift used in post processing. Because continuous monitoring generates such a vast volume of data and some portion of the data commonly exhibits instrument drift, some post collection processing of the data is usually necessary and can be a considerable effort. Some protocols require that data collected by continuous monitors be rejected once instrument drift exceeds 5 percent.

#### **4.1.1 Continuous Monitor Configuration/Station Types**

There are three general types of continuous water quality monitoring station configurations. They include (1) the flow-through (cell) monitoring system that requires a submersible pump to deliver water to sensor(s) mounted in a shelter positioned adjacent to the water body, (2) a configuration in which the sensors are immersed directly into the water body (in-situ) with cables connecting the sensors to the power supply and data recorder housed in the shelter and (3) an in-situ configuration which employs a self-contained sensor, recording system, and power supply (e.g. battery powered datasonde) all located in the sonde (Wagner et al, 2001, Appendix C-3 ). Deployment methods in

flowing water systems usually install the probe through piping anchored in some fashion to the bank or other fixed object (e.g. downstream support structure of a bridge) to protect against loss of the equipment during high flows. Each system has its own advantages and disadvantages in relation to site location and data quality objectives. For those contemplating continuous monitoring stations in their Network, they are referred to Wagner and others (2001) in Appendix C-3 for further detailed discussion of these topics.

## 4.2 Intermittent/Discontinuous Monitoring

Intermittent or discontinuous monitoring (synoptic) of basic water quality parameters is most common. This monitoring is conducted at some regular interval (yearly, quarterly, monthly etc.) and may use either single parameter or multi-parameter instruments for in-situ measurements or measurement of subsamples after depth- or width-integrated samples have been composited in a cone or churn sample splitter. Monitoring at these stations require regular visits by sampling technicians to manually collect field parameters and any other site-specific sample suites selected by the Network for lab analysis. There is a trend in water quality monitoring among federal and state agencies to shorten the intervals between sample collections to improve the overall usefulness of the data (e.g. in time series analysis). This recognition is the result of the valuable information apparent in samples obtained with greater regularity and the short interval variation in parameter measurements that are apparent from continuous monitoring. Therefore, establishing trends from sampling data collected synoptically or discontinuously can be very difficult to do conclusively.

There are also several conditions where intermittent monitoring may better achieve the desired data objectives and goals. This is particularly true where the characterization of longer-term events in water bodies having relatively stable parameter measurements is an important consideration. Less expensive discontinuous monitoring can provide a wider range of parameters using sampling suites under a variety of flow conditions. Intermittent monitoring also does not generate the large volume of data that must be reviewed and corrected that continuous monitoring data does, so can be less costly to handle and less labor intensive to manage. This is but another reason why a thorough **understanding and assessment of one's data objectives and goals and natural variability of the system to be monitored** is such an important step prior to the design of a monitoring system.

## 5.0 Required Field Measurement Parameters

The purpose of field measurements is to better represent the natural condition of the surface water system at the time of sampling and thus avoid measurement errors of unstable parameters potentially introduced by changes to the sample during offsite shipment to a lab. Developments in sensor (single parameter probe) and sonde (multiple bundled sensors) technologies over the last several years has made it possible to measure several basic water quality parameters (up to 11) on a routine basis. This is particularly

true with the development of multiparameter probes or sondes, which facilitate multiple in-situ measurements (temperature compensated) to monitor parameters indicative of a water body's general health. Although measurement of several basic water quality parameters in the field has become routine, considerable care is required to ensure that the data is representative and sources of potential measurement error are minimized.

WRD staff, coupled with input from freshwater and marine/estuarine workgroups have identified four (4) basic field water column measurements and their units of measure for reporting purposes. Collection of this core parameter suite or basic physical/chemical information about a water body will be **required** at all freshwater and marine/estuarine monitoring sites to ensure some consistency and comparability of the Servicewide data set.

The field-measured parameters must all be reported as **temperature compensated values** in reporting units as follows:

1. **Temperature** (units of °C or Celsius, round to nearest degree or tenth of a degree as warranted by instrument)
2. **<sup>a</sup>Specific Conductance\*** in units of microsiemens per centimeter (µS/cm) rounded to two or three significant figures when justified (freshwater)& Salinity mS/cm (marine)
3. **pH\*** (std pH units rounded to nearest 0.1 pH unit)
4. **Dissolved Oxygen (DO)\*** (units of mg/l rounded to one decimal place unless otherwise justified)

a Always to include reporting of raw conductivity

\*Temperature compensated value

Note: WRD selected freshwater Specific Conductance (conductivity at 25° C) and marine Salinity (Practical Salinity Units at 15° C) for display and recording because these temperature compensated forms of conductivity offer field personnel the best direct and immediate comparison of this measurement with past data (i.e. with temperature effects removed to eliminate up to a 3% conductivity measurement change per degree C solely due to temperature). However, field probe measurements of Specific Conductance, Salinity and Total Dissolved Solids (TDS) are all “derived” measurements from (raw) conductivity meaning the instrument has a built-in algorithm in its software to automatically compute these “derived” parameters from conductivity. Not all manufacturer’s instruments use the same built-in algorithm to obtain these “derived” values. For this reason, along with the Specific Conductance measurement (freshwater condition) and the Salinity measurement (marine/estuary condition), **raw conductivity values should always be collected and reported** along with the recommended derived parameter.

In addition, **at flowing freshwater sites**, a 5<sup>th</sup> parameter-**qualitative flow**, shall be estimated at a minimum in lieu of the preferred quantitative flow measurement. This **flow estimate** shall be based on percentage of bank full (**low/base flow** when < 25% of bank full condition, **intermediate** from 25% to 75% of bank full, **high** > 75% bank full and **over bank/flood** when exceedence of bank full condition is manifested. However, a **quantitative flow** measurement is always preferred and should be obtained at all

monitoring stations where it is feasible and cost-effective to do so. Quantitative flow is necessary for Total Maximum Daily Load (TMDL) computations and in many instances to flow adjust concentrations in statistical analysis of data for temporal trend analysis. Monitoring sites on ephemeral streams with standing water may be reported as **water present but no flow** and dry stream beds simply as **dry**.

**Quantitative flow measurements** will most typically be obtained by locating monitoring stations at **existing gage sites, establishing a gaging station at new monitoring stations** or placing a staff gage and **developing a set of rating curves** under various flow regimes throughout the year at the monitoring site. It is anticipated that 90% or more of a Network's flowing water monitoring sites will include a **quantitative** flow measurement due to the importance of this parameter to compute loading and properly evaluate trends and other physical/chemical data.

**At non-flowing/still freshwater sites**, WRD requires that a **vertical profile of the water column for the core parameters** be conducted to characterize any stratification of the water body. In addition, an **estimate of the water body stage or level** is required as the 5<sup>th</sup> parameter in lieu of an actual measurement (preferred). Typically, stage/level information is available from the water body managing agency/owner or a cooperator (e.g. BLM, COE, BOR, and USGS) who may regularly record these data. The estimate of stage/level shall be based on the **normal yearly range** of the water body's stage/level using similar divisions for estimated flow for flowing water bodies (i.e. low <25%, intermediate 25% to 75%, and high implying the water body is at a level > 75% of yearly range etc.) with a flood stage for standing/non-flowing water defined as that condition indicative of a significant exceedence of the normal yearly range for stage/level.

Finally, at freshwater sites, a minimum of **1 digital photograph is required** to document each monitoring site (1 picture at a minimum but seasonal/yearly documentation is recommended where feasible). Metadata to be collected at freshwater monitoring sites required for upload of data to STORET and required by WRD to will be addressed in Part E of this guidance.

**At marine sites**, ionic strength expressed as conductivity and the derived parameters of salinity (as Practical salinity Units in ppt.) and Specific Conductance (mS/cm) will be reported along with Temperature (°C), Dissolved Oxygen (mg/L) and pH (Std. units) (see "Core Water Quality Monitoring Parameters for Marine and Coastal National Parks" at <http://science.nature.nps.gov/im/monitor/deskref.htm>). Additional required metadata beyond that expected for freshwater sites (location, time of day, water body type, measurement method, and sample type, depth, meteorological data, habitat description etc. per list in Part E), but unique to marine sites include:

1. **Tidal stage**, time related to high and low tide times, and whether tide is flowing in (flood tide) or out (ebb tide)
2. **Estimated wave height**

(see Marine core parameters work group recommendations for suggested additional metadata at <http://science.nature.nps.gov/im/monitor/deskref.htm> )

In freshwater monitoring, two (2) additional field measurements (biomonitoring, and alkalinity or acid neutralization capacity - ANC) are also singled out for discussion because of their widespread importance and utility in Vital Signs monitoring. These parameters are highly recommended and should at least be considered by Networks at all appropriate monitoring sites. Some other field observations (habitat) and measurements more commonly made in the laboratory (nutrients, bacteria, toxics, water hardness etc.) are also important and widely monitored. The latter are discussed in more detail in Part D and Part B of this guidance at <http://science.nature.nps.gov/im/monitor/protocols/wqPartB.doc> ). Selection of these and other water quality parameters to be monitored should be based on Network-wide or site-specific concerns identified in the planning and assessment phase of the Vital Signs monitoring program and **a parameters ability to reflect anthropogenic caused change over the natural variation of background.**

Factors considered in the selection of the required field measurements were a parameter's (1) utility in vital signs assessment, trend analysis, and as a basic measure in determining overall health and characterization of a water body, (2) likelihood of meeting or addressing some regulatory requirement, beneficial use, numerical or regulatory criteria (3) ease to acquire based on current and anticipated future technological developments (4) commonality with other monitoring programs and historical data sets and (5) the need for some measure of consistency and comparability of parameters (core suite) in the Servicewide data base. Finally, the incremental cost to acquire these core parameters once a sampling team has been mobilized to a site to perform other monitoring is almost negligible.

## 5.1 Guidance and Rationale for Selected Field Measurements

This section of the field guidance discusses in more detail:

- 1) The required or “core” set of basic water quality parameters to be collected by all Networks at all water quality monitoring stations and their rationale.
- 2) How the selected parameters may be collected in the field (i.e. by a single multiparameter instrument-preferred or by multiple individual instruments) and the basis for their selection (i.e. largely chosen to provide relatively standard and cost effective baseline information to support a minimum data set for purposes of Servicewide method consistency, data quality, and data comparability over the long term).
- 3) General guidelines and standard/accepted field procedures or their references that are generally applicable to all Networks



- 4) Those field methods, field practices or equipment options, which are generally most applicable (or where such information is best found) to water quality monitoring under the Vital Signs program
- 5) Metadata requirements of STORET, and the metadata associated with the collection of field parameters (see also Parts B and E of the WRD Guidance)

Field measurements are made onsite to determine the physical or chemical properties of a water body. Chemical and physical parameters selected for field measurement are typically the least stable or most subject to change during handling and transportation. For this reason, cost effective field measurement technologies with acceptable accuracy for most monitoring applications have been developed and implemented historically. Because of parameter instability, the required four (4) parameters selected for field measurement should not be performed in the laboratory.

Sensor-based, field water quality measurements are generally made in one of two ways. Either a single parameter instrument or multiparameter probe device is placed directly into the water body (in-situ) and a measurement is made, or a single parameter probe measurement is made on a sub sample of a composited sample that has been run through a sample splitter (e.g. churn or cone splitter). Because **in-situ measurements** avoid any changes that can result from removal of the sample from its environment, that is generally the preferred method. However, the sample location selected should be representative of the water body and this should be documented in cross-sectional measurements (e.g. in streams) or with profiling (e.g. in lake).

The USGS has developed procedures for arriving at representative in-situ values for water bodies that may not be, or have not yet been determined to be homogeneous. Such water bodies may not be well represented by a sample collected from a single sample location (grab sample) chosen to represent that water body (e.g. centroid of a flowing stream). These procedures, the Equal Discharge Increment (EDI) method and the Equal Width Increment (EWI) method either (1) divides the stream into increments of equal discharge or (2) divides the stream cross-section into increments of equal width, respectively. Representative field parameters are then taken as the mean or median of the measurements collected at the midpoints of each increment. Alternatively, if the profile of the parameters to be measured indicates the stream is well mixed (e.g. differ less than 5% in pH and specific conductance measurements along a transect), a single measurement point at the centroid of flow (typically selected in a riffle area) can be used to represent field measurement values of the stream's cross section (NFM Section 6.0.2 in Appendix C-1).

Quality assurance protocols are a means to ensure data collected is as representative of the natural environment as possible. Quality assurance protocols are required in all data collection efforts under this long-term monitoring program. They include implementing good field procedures and quality-control checks. This requires that **(1) field measurements be made only with calibrated instruments, (2) field teams maintain a permanent instrument log book recording calibrations and**

repairs, (3) the appropriate instruments be tested and/or calibrated before leaving for the field, and at a minimum, DO and pH be calibrated again in the field at the monitoring station immediately prior to data collection (per Table C-1), (4) all manual recorded field measurement data be collected on field forms and that automatically recorded data be captured electronically and the equipment used be documented on field forms, and (5) complete records are maintained for each uniquely identified sampling station and all supporting metadata be recorded appropriately (field forms or electronically).

There is no substitute for complete and accurate record keeping of field derived data. Data and metadata (data about data) must be captured by the field technician and recorded either on paper or electronically. Electronically captured data should be backed up to a second drive or disk as soon as possible. Field recorded data should include field measurement data, methods used, and metadata. Also, the equipment used (brand and model number) and calibration information should be indicated on appropriate field forms and in the field logbook. Examples of USGS water quality field inspection forms and metadata associated with a station description are found in Appendix C-3 (continuous monitors) and Appendix C-5 (example field forms). States may also have specific field forms and required meta data and these forms and meta data should be used/included when monitoring in a regulatory context. Part E of this guidance also provides a list of required and recommended/optional metadata to be recorded under the water quality component of the Vital Signs Program.

#### **5.1.1 General Considerations in Determining the Four (4) Required Field Parameter Measurements Plus Qualitative/Quantitative Flow**

The bundling of water quality sensors for use as a multiparameter sonde is becoming more commonplace in water quality monitoring and the trend of increased use is likely to continue as technologies develop further, their operation and maintenance becomes simpler, and as sensor reliability improves. As a practicality and in acknowledgement of this trend, the focus of this guidance will be on field deployment (manual/intermittent and automated/continuous monitoring) of multiprobe equipment. Also, in-situ measurement of several field parameters is more readily obtained using multiprobes because vertical and horizontal profiles of multiple parameters may be obtained in a single transect of the water body (e.g. stream). Therefore, the guidance that follows recommends procedures that emphasize and incorporate the more recent technological advances in multiparameter probe developments and related field techniques.

**WRD requires that a minimum of four (4) basic water column parameters be measured** at all monitoring stations in all Networks to meet Servicewide minimum data collection needs. If a multiparameter probe or sonde is used to collect this core data set, oftentimes one or more additional sensors may be available for the Networks to deploy (e.g. turbidity) to meet specific monitoring needs or data objectives of the Network.

In addition to the 4 water column parameters (**temperature, specific conductance, pH and dissolved oxygen**) and either a **qualitative estimate of flow** or a **quantitative flow measurement** (preferred), WRD suggests that the Networks consider selecting one or more additional water quality sensors (e.g. turbidity, ammonia, nitrate,) if field measurement of these parameters meet Network needs, data quality objectives or site-specific monitoring objectives. At this time, most, smaller diameter multiparameter sondes (< 2") are generally limited to 6 simultaneous measurements (temperature, specific conductance, pH, DO, ORP and vented or non-vented level). However, some smaller diameter multiprobes do now offer turbidity (Hydrolab Quanta and In-Situ MP9000). Internal algorithms are used to derive salinity, specific conductance, and total dissolved solids values from the conductivity (raw) measurement based on several assumptions as to the type of water and ionic content (usually that the natural water approximates that of a KCl standard solution). Typically the applied algorithm selected by the instrument manufacturer is from a recent edition of Standard Methods. Alternatively, raw conductivity values may be used to calculate salinity, specific conductance and TDS during data processing (sometimes the preferred approach for marine monitoring) when the data is uploaded to STORET.

Larger diameter sondes ( $\cong 3''$ ) may make from 7 up to 10 or more measurements simultaneously from a total of 13 possible sensor options. These include temperature, specific conductance, pH, DO, turbidity, vented or non-vented level, oxidation-reduction potential (ORP), and chlorophyll  $\alpha$ . In addition to this are 2 or more expansion ports for substitution of ion specific electrodes (e.g. chloride, ammonia and/or ammonium-nitrogen, nitrate-nitrogen etc.) and measurement of total dissolved gas. Additional sensor options, sensitivity, and lower detection levels should be anticipated as these technologies develop further. However, **data quality objectives should be specified before selection of probe-based measurement methods for the more stable parameters (chloride, nitrate, ammonia, chlorophyll  $\alpha$  etc.) that do not require field measurement because detection levels are generally not as low as those achieved through laboratory analysis.**

Generally, as the number of desired water quality parameter measurements increase to 4 or more, it is more cost effective and easier to obtain the desired and recommended in-situ measurements and their documentation with a multiparameter sonde and display system that performs measurement, temperature compensation, logs/displays the data real time and captures metadata (time, depth, barometric pressure etc.) simultaneously. This is particularly true from a practical standpoint if multiple in-situ measurements are made at various points and/or at various depths during a stream transect or at various depths in a standing water body (e.g. lake). Multiparameter water quality devices and data loggers are specifically designed for use in monitoring programs. The sondes typically come equipped with various accessories and components to facilitate field use and capture of data into large files, are highly portable, come with internal clocks, and are supplied with cables of various lengths offering considerable flexibility in parameter measurement in time and space. They also provide **temperature compensated measurements** using a highly accurate, factory-calibrated thermistor.

Temperature, and DO measurements are only representative when performed in-situ and should never be performed on sub samples. Specific conductance and pH measurements may also be affected by temperature change and are subject to greater error when not made in-situ. In-situ measurements of turbidity are also preferred due to the possible settling out of particles causing error (low bias) during the turbidity measurement of sub samples or changes that can occur (e.g. low measurement bias from adsorption to walls of container, flocculation of small particles etc.) when re-agitating the sample prior to performing the turbidity measurement on a sub sample.

Of the previously discussed “required” (4) water column measurements plus flow (quantitative or qualitative) and the two highly recommended supplemental field measurements (biological monitoring, and alkalinity or acid neutralization capacity) for consideration at all sites, only the alkalinity and ANC measurements are routinely performed on a sub sample (post sample splitter). No direct-measurement probe technology is available for either of these parameters and they are usually determined most accurately by field titration with a digital titrator. Field measurement of alkalinity/ANC requires a wet chemical method that can be difficult to perform under some field conditions.

The USGS has developed computer software to facilitate the alkalinity/ANC titration in the field (usually done in field vehicle/mobile lab). This allows the titration endpoint to be reached more quickly (personal communication Jim Collins, USGS). Because alkalinity (performed on filtered sample) is a good indicator of a water’s acid buffering capacity (ANC is performed on an unfiltered sample so includes the buffering capacity of the suspended solids fraction), its determination is important under a wide range of conditions. Networks are encouraged to consider including either alkalinity or ANC measurements at most monitoring stations as a basic parameter in characterization of a waters susceptibility to acid input, particularly where air shed monitoring (vital sign) is conducted concurrently.

Field personnel should be experienced in the use of the water quality probes and should have become familiar with the manufacturers instructions for calibration and utilization of the specific equipment planned for use in the monitoring/sampling effort. Experience in equipment handling, calibration, and use/field deployment of the sondes/probes is best obtained through a combination of apprenticeship, vendor workshop training, and through testing of and gaining some familiarity with the equipment at the office/lab prior to entering the field. Becoming familiar with the **manufacturer’s equipment operation and maintenance manual** is also extremely important. Improper handling and storage of the multiparameter sonde and sensors can lead to equipment damage or premature sensor failure. Problems with probe or sensor function, their failure or damage, is best avoided by following the manufacturers instructions carefully. Typically, an equipment vendor also provides a 1-800 telephone number for additional assistance in troubleshooting should problems arise with equipment while in the field. Direct communication with the equipment manufacturer can be an important source of troubleshooting and problem resolution of equipment

malfunction in the field. For this reason, a **cellular phone** should be a standard component of the field equipment to save cost and facilitate trouble shooting in the field.

Due to the large variety of currently available single and multiparameter field instruments and their continuous updating or replacement by newer technologies, no one vendor or single instrument can be recommended. However in the area of multiparameter probes, both Hydrolab and Yellow Springs Instruments (YSI) probably have some of the longest track records in multiparameter probe manufacturing, sonde and sensor research and development, and in probe deployment under a variety of conditions. These companies also offer **workshops** around the country and training at their various facilities in operation, calibration, and maintenance of their water quality monitoring equipment. In-Situ is a third company that recently expanded its product line into multiparameter water quality monitoring equipment. In-Situ has a long record of product development in the in-situ measurement and continuous monitoring of surface and subsurface water levels related to groundwater hydraulics. Its product line was recently expanded to include the Troll 9000 multiparameter instrument. Overseas-based firms marketing multiparameter equipment include Horiba (Japan) and several European firms. Horiba markets in the U. S. and has recently come out with a new U-20 series of multiparameter probe. Stevens Water Monitoring Systems based in Portland, Oregon, also has recently expanded into water quality monitoring, focusing on longer term equipment deployments.

Software developments in data handling and management of multiparameter data particularly from continuous monitors is also ongoing and an important consideration for Networks in their procurement decisions. Post-processing of continuously monitored parameters to address the more linear changes in data records (e.g. electronic drift and some types of sensor fouling) can be a sizeable time demand. The USGS has developed several computer programs to facilitate the post-processing of continuous monitoring data. Best results are generally achieved when the individual most familiar with the conditions under which the data was acquired, is also responsible for the post-processing. WRD anticipates that appropriate **post-processing of continuous monitoring data would occur at the Network level** before monitoring data is supplied for upload into STORET.

Network personnel responsible for the selection and procurement of field probes should become informed as to what instrumentation and associated software is currently available on the market and make decisions as to what best meets the Network's long-term water quality monitoring needs and objectives. To assist in that effort, WRD arranged for a demonstration and testing of three (3) manufacturer's multiparameter probes (In-Situ, YSI, Hydrolab) to be deployed (side by side) over a 6-month period at four Parks around the country. WRD will assist wherever possible in providing information to Networks on these water quality instruments based on the outcome of this testing, so that better informed instrument procurement decisions might be made. When possible, WRD also will perform limited evaluations of new multiparameter instruments that may enter the marketplace. Preliminary information was provided on results of the

multiparameter instrument demonstration at the Nov. 2002 WRD sponsored water professional's biennial meeting held in Fort Collins, Colorado.

Results of lab testing of some of these instruments by the USGS Hydrologic Instrumentation Facility are currently available on the web at [www.hif.er.usgs.gov/ofa](http://www.hif.er.usgs.gov/ofa) (go to pub, instrument news, and use search function for instrument brand). Also field testing of multiparameter equipment is being done by the USGS over the summer of 2002 in association with nutrient sampling under the NAWQA program (personnel communication Holly Weyers, USGS). Increased competition among vendors has led to rapid technological developments, expansion of multiprobe product lines and an increasing array of monitoring options available to fit the growing monitoring needs of Networks. To take greatest advantage of these competition induced technological developments, it is recommended that Networks postpone instrument procurements until a few months before Networks begin steps to implement their monitoring program.

#### **5.1.1.1 General Issues in Sensor-based Measurement of the Four (4) Required Water Column Parameters and Instrument Calibration**

Calibration of conductivity (for the specific conductance measurement), pH and DO is best performed in the field just prior to making measurements to ensure data is most representative. A field check of the temperature probe (thermistor) against a **NIST certified digital thermometer** is also generally sufficient and the preferred check method. Use of a NIST certified liquid-in-glass (alcohol) thermometers tend to have a short life expectancy when used for field check purposes (personal communication, Bob Boulger, USGS) so should be avoided. Field calibrations of pH and DO should be done immediately preceding and at the completion of sampling at each monitoring station. Measurement bias resulting from instrument drift or other causes may be determined in this way and could be significant under some circumstances if several hours have passed since the initial calibration. A daily calibration for conductivity (specific conductance) is generally sufficient unless the stability of the sensor is in question. It may take from 15 to 20 minutes for a multi-parameter probe to be calibrated for specific conductance, pH, and DO by an experienced technician. Adverse weather or below freezing conditions may require that calibrations be performed in the field vehicle and measures be taken to protect probes from freezing when not submersed in the water body.

Temperature calibrations on multiparameter probes are important because several of the other parameters are automatically temperature compensated. It is usually sufficient to check the highly accurate temperature thermistors used in multiparameter probes against certified thermometers upon the multi-parameter probes purchase and then prior and subsequent to each field use. The DO measurement is sensitive to changes in location due to barometric effects caused by changes in altitude and barometric pressure variation (physical movement between pressure isobars) when moving between monitoring stations. Sensors or the instrument electronics may be affected by electronic drift, temperature extremes, pressure variation (air transport), jostling of the instrument during transport to the field or their deployment in electrical fields (e.g. near power

lines). These and other conditions can cause non-representative readings, instrument error, or equipment failure. These are but a few of the reasons for completing an initial and a post-calibration check for pH and DO at each monitoring station. An air tight Pelican case equipped with a pressure release valve/knob and cutout foam padding to fit dimensions of various equipment components works well for protection of multiparameter probes from various environmental effects during transport to and from the field.

Each sensor requires some period to stabilize/equilibrate to the temperature of the water body and warm-up prior to measurement. Typically, **a warm-up time of two minutes is necessary for individual sensors in continuous deployments**. The pH and DO measurements require one or more ion specific transfer/reactions to occur at the sensor boundary/membrane. Generally the DO measurement requires the longest to stabilize. **Stabilization of the DO measurement may take anywhere from 5 to 15 minutes when making synoptic measurements** and can be very probe (manufacturer) or water body dependent. In-situations of low ionic strength water [low total dissolved solids (TDS) with very little buffering capacity], the pH measurement may never stabilize and a mean or median pH value must be taken from a range covering several tenths of pH units. The USGS has provided **stabilization criteria for recording field measurements in Table 6.0-1 of the NFM**. Stabilization criteria along with other recommended instrument specifications are reproduced in Table C-1 for reference. Some vendors offer **specific pH probes for use in waters of low ionic conditions** to achieve stable measurements.

**Table C. 5-1** Stabilization criteria (from NFM, 1998) and WRD recommended instrument specification criteria for recording field measurements

Standard Direct Field Measurement	Stabilization Criteria For Measurements (variability/repeatability should be within the value shown)	Recommended Instrument Specifications A. Range B. Resolution/Sensitivity** C. Accuracy***
<sup>1</sup> Temperature: Thermistor Thermometer Liquid-in-glass Thermometer	$\pm 0.2^{\circ}\text{C}$ $\pm 0.5^{\circ}\text{C}$	A. $-5$ to $+45^{\circ}\text{C}$ B. $0.01^{\circ}\text{C}$ C. $\pm 0.15^{\circ}\text{C}$
<sup>2</sup> Conductivity (Specific Cond.) When $\leq 100 \mu\text{S/cm}$ When $> 100 \mu\text{S/cm}$	$\pm 5$ percent $\pm 3$ percent	A. 0 to 100,000 $\mu\text{S/cm}$ B. 1 to 100 $\mu\text{S/cm}$ (range dependent) C. $\pm 0.5\%$ of reading $+1 \mu\text{S/cm}$
<sup>3</sup> pH: Meter displays to 0.01	$\pm 0.1$ unit	A. 0 to 14 pH units B. 0.01 pH unit C. $\pm 0.2$ pH unit
<sup>3</sup> Dissolved oxygen: Amperometric method	$\pm 0.3$ mg/L	A. 0 to 50 mg/L B. 0.01 mg/L C. 0 to 20 mg/L; $\pm 2\%$ of reading or 0.2 mg/L, whichever is greater
<sup>*2</sup> Turbidity: Turbidometric method in NTU	$\pm 10$ percent	A. 0 to 1000 NTU B. 0.1 NTU C. $\pm 5\%$ of reading or 2 NTU Whichever is greater; depth limit of 200 ft.

- \*Measurement is not required (i.e. not a “core” parameter)
  - \*\* Resolution/Sensitivity is a data quality indicator related to detection limits but typically handled differently for field probes than for laboratory parameters. For more information, see Part B  
(<http://science.nature.nps.gov/im/monitor/protocols/wqPartB.doc>).
  - \*\*\*In the case of field probes, accuracy is typically a “best case” maximum deviation from known correct values (typically based on comparisons with known NIST certified reference materials or standards). True accuracy is a combination of high precision and low bias (see Part B for more details).
- <sup>1</sup> Recommended sensor calibration is quarterly
- <sup>2</sup> Recommended sensor calibration is daily
- <sup>3</sup> Recommended sensor calibration is at beginning and end of sampling at each station (twice a day minimum)
- \*Note that measurement stabilization criteria are not the same as Measurement Quality Objectives (MQOs) listed in the “Core Water Quality (Vital Signs) Monitoring Parameters for Marine and Coastal Parks” produced by the marine work group.



### 5.1.2 Other Important Field Measurements for Widespread Consideration in Monitoring

In many instances, Networks should consider supplementing multiprobe water column measurements of the core parameters and quantitative or qualitative flow (flowing water case) or level (non-flowing water case) measurements with other highly recommended **field data** from biomonitoring, and **alkalinity** /ANC measurements. Although these parameters are neither as universally applicable nor as inexpensively acquired as the probe-based core set of required parameters, they can be a critical component of vital signs monitoring in many situations and should therefore at the very least, be considered for inclusion at each monitoring station. These additional field measurements are highlighted and discussed here for that reason. Some explanation or basis for their omission at appropriate monitoring sites (e.g. wadeable streams) should be specified in the detailed monitoring plan.

WRD recommends that the physical parameter of **flow/discharge** be quantitatively measured at essentially all monitoring stations involving a flowing water condition (stream, river etc.) or a nearby gaging station should be identified as a source of this data. When it is not possible or infeasible (cost prohibitive) to obtain a **quantitative flow measurement**, Networks must at a minimum, **estimate flow** based on the best information available and per the general guidance provided in Section 5.0 of this document.

Some **biological assessment parameter** should also be an important consideration in many water-quality monitoring situations (see Part B Section IV) of this Guidance for more detail). This latter vital sign is often times the best means of determining impacts or changes to water quality that may not be manifested by physical or chemical monitoring of the water column. However, biological monitoring is prone to high variance due to several factors (climate and other changing conditions, investigator bias/subjectivity) that can lead to high measurement uncertainty that often exceeds changes due to anthropogenic effects. For this reason, the various forms of biologic monitoring should be carefully weighed, their basis for selection well-documented, and an effort made to understand measurement uncertainty in the biologic parameter monitored.

Finally, **alkalinity and/or acid neutralization capacity** of a water body should be considered for measurement using field titration methods, as these measurements are the prime indicator of a water body's susceptibility to acid inputs. They are a particularly important parameter(s) to measure in areas where acid mine drainage or acid precipitation is a potential concern or buffering capacity of a water body is low. Although lab determinations of alkalinity are acceptable, the field determination is preferable and generally regarded as more representative.

Flow/discharge is a very important physical parameter of the water body that can strongly affect or show direct correlation to both biological and chemical parameters. For

that reason, although not required, quantitative flow measurements are “highly recommended” by WRD at all Network monitoring stations characterized by flowing water. A quantitative flow measurement requires different expertise, measurement methods, and equipment from that used to measure other chemical/physical parameters. Also rating curves must be established for a site and re-verified on a regular basis. Thus, a quantitative flow measurement is not as readily obtained along with the other four (4) core parameters that share a common probe-based technology and may require significant additional resources. Neither is the measurement of flow/discharge generally applicable to still or standing water bodies. In recognition of these unique qualities and added requirements (cost, effort level, equipment, and expertise) when quantitatively measuring flow/discharge, and despite its recognition as a crucial component of flowing water bodies, WRD requires that only a qualitative estimate or assessment of flow be obtained at all monitoring stations. However, this should be viewed by Networks as only meeting a minimum requirement and that a quantitative flow measurement is strongly recommended and should be acquired at most flowing water sites.

It is important that Networks realize that the interpretation of data from the 4 core water column parameters and most other Network/site-specific parameters selected can be affected simply due to changes in flow/discharge. Flow is also a key component in calculating chemical and physical loading of a flowing water body that is the basis for Total Maximum Daily Load (TMDL) studies. WRD thus assumes Networks will recognize and acquire quantitative flow/discharge data at most, if not all monitoring stations characterized by flowing water conditions.

There are other important field measurements that may be considered in place of more costly laboratory measurements, providing data quality objectives are met. Generally there is some compromise in accuracy and precision with such sampling/measurement methods relative to a lab analysis. Field measurement of **nutrients, specific cations or anions** (e.g.  $\text{Fe}^{+2}$ ,  $\text{Cl}^-$ ) and some **bacteriological testing** are just a few examples of tests that may be analyzed relatively less expensively with either field test kits or multiprobes. When considering such field-testing, thought should be given to whether or not the precision and bias inherent in some of these methods (screening level?) are sufficient to meet sensitivity, precision, and bias data quality objectives. Sometimes screening level methods are “good enough” if they meet specified data quality objectives, and are “accurate enough” to answer specified questions (see Part B Section VI of this Guidance). Interferences of other dissolved constituents typically also have more of an effect on accuracy when using probe-based measurements versus lab analytical methods.

### 5.1.3 In-situ Versus Subsample Measurements

Subsample measurements are those produced from samples collected and composited using discharge or depth- and width-integrating sampling methods. These methods are used to collect and composite samples that can then be subsampled (e.g. run through a churn or cone sample splitter) for some field measurements (e.g. alkalinity) or more typically to obtain representative composited samples for offsite lab analysis. The

USGS has adopted two integration methods for compositing depth-integrated samples from a flowing water body that may or may not be well mixed. The methods are equal-discharge increments (EDI) and equal-width increments (EWI). In addition to the discussion in the NFM, the USGS has produced a **Field Guide for Collecting and Processing Stream-Water Samples for the National Water-Quality Assessment Program (Shelton, 1994)** which discusses equipment needs, sample collection and processing methods, field analyses, documentation and QA/QC procedures used by NAWQA (Appendix C-2). This practical field guide is an excellent supplement to the NFM and should be consulted by Networks in preparing their detailed, water quality monitoring plan, in addition to any State-specific water quality sampling protocol guidance. This USGS field procedures guide and an excellent example of State-specific (Texas) guidance (the latter oriented toward monitoring within a CWA regulatory regime) are available on the net at <http://water.wr.usgs.gov/pnsp/pest.rep/sw-t.html> and <http://www.tnrc.state.tx.us/admin/topdoc/gi/252/swqmproc.pdf>, respectively.

In-situ measurements are those collected by placing a particular sensor or bundle of sensors (sonde) directly into a water body and recording the result. In-situ measurements are recommended for all four (4) of the “core” set of water column measurements that can be made with a probe. These include the four basic or primary parameters to be collected Servicewide (temperature, specific conductance, pH, and dissolved oxygen). Where it is appropriate, desirable, and data quality objectives are not compromised, other parameters may include turbidity or those from an additional list of optional parameters that may also be collected with a probe/sonde (e.g. Eh/ORP, chlorophyll  $\alpha$ , ammonia/ammonium, nitrate, chloride, total dissolved gas, and depth/level).

Prior to initial sampling at a site and again 3 to 4 times per year, it is recommended that a stream profile of field measurements (velocities, specific conductance, temperature, pH and DO) be obtained. By recording observations from several verticals and depths in the cross section, the uniformity of these characteristics may be ascertained and used as guides in selecting an adequate number of verticals for obtaining a representative sample. If it can be established that these integrated measurements (pH and specific conductance) do not vary outside the parameter stabilization criteria shown in Table C-1 for the measurement during times of both peak and base flow, then depth and width integrated field probe measurements may be discontinued and replaced by a single measurement for each parameter at a representative point such as the centroid of the flowing water body (i.e. typically the midpoint and mid depth in a riffle section or a section of stream reach where a pool transitions to a riffle and good flow is present).

## 5.2 Water Quality Instrument Sensors Used in Field Measurements

### 5.2.1 Introduction

This section discusses issues related to sensor theory, calibration, units of

measurement, measurement methods, accuracy, reporting, and maintenance, cleaning and storage for the sensors used in obtaining the four (4) required field parameters. Other probe-based sensors that may be selected by Networks on a site-specific basis are also addressed in varying degrees based on their likely utility or deployment frequency by Networks under the Vital Signs program.

### **5.2.2 Water Quality Instrument Sensors Used in Multiprobes**

General parameter information and sensor theory, calibration, measurement methods, accuracy, general probe operation, maintenance, and storage procedures for the temperature, specific conductance, pH, dissolved oxygen, and other available sensors (e.g. turbidity) are discussed in this section. Because the utility of the turbidity sensor in monitoring situations is not as widespread at the basic four, WRD chose to provide Networks the maximum monitoring flexibility by limiting the core set of water column parameters to four (4) to allow Networks to select any added sensor-based water quality measurements which best meet site-specific or Network-wide needs within their budgets. Additional sensor options will be subject to the multiparameter technology deployed, but typically will include nitrate-nitrogen, ammonium/ammonia-nitrogen, chloride, total dissolved gas, and chlorophyll a for larger diameter datasondes or turbidity and/or a few other sensors for the smaller diameter or minisonde instruments. Sensors for depth, or vented level (shallow, intermediate, deep), and oxidation-reduction potential are also available as separate sonde ports or in conjunction with other sensors in most sondes.

Some typical reported sensor performance specifications (range, resolution, and accuracy) of vendors are shown in the Table C.5-2. These likely reflect optimal conditions of sensor operation as a function of calibration, operator ability and technique, and controlled conditions under which the measurements were made (e.g. the end of the production line prior to shipment to the purchaser). Therefore, such specifications may not be widely or consistently achievable in the field where measurement conditions and operator skills may vary widely. They are provided herein so that some general comparison with lab methods can be performed in a relative sense to determine if probe-based measurement methods potentially meet data quality objectives. Verification of individual sensor performance and instrument specifications should be undertaken with the instrument vendor before purchasing as they can vary among vendors and instruments.

**Table C. 5-2 Some typical sensor performance specifications of multiprobes**

<b>Sensor</b>	<b>Range</b>	<b>Resolution</b>	<b>Accuracy*</b>
Temperature	-5 to 45 °C	0.01 °C	±0.15 °C
Conductivity	0 to 100 mS/cm	0.01 to 0.1 mS/cm (range dependent)	±0.5% of reading + 0.001 mS/cm
pH	1 to 14 units	0.01 unit	±0.2 units
DO	0 to 50 mg/L	0.01 mg/L	0 to 20 mg/L; ±0.2 mg/L; 20 to 50 mg/L; ±0.6 mg/L
Turbidity	0 to 1000 NTU	0.1 NTU	± % of reading or 2 NTU whichever is greater
Salinity	0 to 70 ppt	0.01 ppt	± 1% of reading or 0.1ppt, whichever is greater
Nitrate-nitrogen	0 to 200 mg/L	(0 to 1 mg/L-N (range dependent))	± 10% of reading or 2 mg/L whichever is greater
Ammonium-nitrogen	0 to 200 mg/L as N	± 10% of reading or 2 mg/L whichever is greater)	± 10% of reading or 2 mg/L whichever is greater
Ammonia	0 to 200 mg/L as N	± 10% of reading or 2 mg/L whichever is greater	± 10% of reading or 2 mg/L whichever is greater
Chloride	0 to 1000 mg/L	0.01 to 1 mg/L (range dependent)	± 15% of reading or 5 mg/L, whichever is greater
ORP	-999 to 999	0.1 mV	± 20 mV
Barometric Pressure	0 to 16.5 psia (854 mm/33.6 in Hg)	0.1 mm Hg or 0.01 in. Hg	± 0.3% FS (2.54 mm Hg, 0.1 in Hg)
Vented Level w/higher accuracy	0 to 30 feet (0 to 9 m)	0.01 feet (0.0003 m)	± 0.01 feet (0.003 m)
Medium depth	0 to 200 feet (0 to 61 m)	0.001 foot (0.001 m)	± 0.4 foot (0.12 m)
Shallow depth	0 to 30 feet (0 to 9 m)	0.01 foot (0.001 m)	± 0.06 foot (± 0.02 m)

\* Note: Accuracy specifications reflect the uncertainty in measurement of the instrument and sensor in combination only and not other factors that can affect accuracy such as environmental factors (field) and field personnel's ability to calibrate and operate the instrument using good measurement protocols. In most instances this table reflects specifications new instruments must meet prior to shipment by the vendor (YSI in this case) to a purchaser. Over time, some degradation of sensor accuracy should be anticipated and sensors will need to be replaced.

### 5.2.2.1 Temperature

Temperature is the degree of heat (warmth or coldness of a substance) measured on a definite scale referenced to some physical phenomenon such as expansion of mercury (liquid thermometer), change of electrical resistance (thermistor), or intensity of radiation.

Temperature of both water and air is a key field measurement at all monitoring sites and is essential information to water data collection. Water temperature is measured because rates of biological and chemical processes are strongly influenced by temperature and numerous aquatic organisms are dependent on certain temperature ranges for optimal health. For example, temperature is a key parameter in assessing the suitability of a water body (e.g. stream) for particular fish species and thus in determining its appropriate beneficial use. Because temporal variation in temperature can be significant, intermittent temperature monitoring (stations) can be problematic and use of continuous recording devices is a preferred means of eliminating these sampling problems (MacDonald et al., 1991).

Temperature variation in water bodies may be from a variety of anthropogenic and natural causes. These include point source discharges (POTWs, power plants, storm sewers, factories etc.), man-made impoundments, shade vegetation (or its removal) along embankments, groundwater inflow, density segregation, (e.g. lakes/reservoirs) and near surface effects of warming by sunlight. In a flowing water setting, a cross-sectional temperature profile should be made at a monitoring station at times of base flow and peak flow to determine temperature variability. A submersible thermistor thermometer typically works best for this purpose. In a still water setting (e.g. lake), vertical profiling of the water column is being required to establish any temperature related stratification. Because fresh water is most dense at 4 degrees Celsius, many lakes will “turn over” one or more times a year as surface waters cool in the fall and pass through this key temperature. Multiparameter monitoring has documented how temperature and other key parameters can change quite rapidly in conjunction with lake turn over.

#### 5.2.2.1.1 Measurement Theory

Specific conductance, pH, Eh/ORP, dissolved oxygen, and even turbidity measurements are temperature compensated. Compensated parameter measurements are those adjusted to a standard temperature, **typically 25° C**. **Salinity** is unique in that it is temperature **compensated to 15° C** in its derivation from conductivity because this temperature more closely reflects the average condition of sea water. An algorithm designed into the software systems of most multiparameter instruments now available does these adjustments automatically. **Temperature compensation** or removal of the effect of temperature (variable) on data output facilitates parameter comparison and trend analysis of multiple records of longer-term data (i.e. removes this measurement effect/variable). Accurate temperature measurements are thus very important because any temperature error (although of usually slight effect except for specific conductance) compounds the measurement error for the temperature compensated parameters. The

measurement of dissolved oxygen is affected by temperature in yet another way. The amount of dissolved oxygen that water can contain at saturation varies inversely with temperature so the maximum dissolved oxygen concentration at saturation (mg/L) is higher in colder waters.

WRD recommends that the three (3) other required water column parameter measurements (i.e. conductivity, pH, DO) plus turbidity, be measured as temperature compensated values. When temperature compensated values are not measured automatically (e.g. in contrast to measurements made with most multiprobes), they should be corrected using a table or noted as not being temperature compensated values in the metadata. For the reasons stated above, use of non-temperature compensated sensors should generally be avoided when a sensor option exists for temperature compensation.

#### **5.2.2.1.2 Calibration and Units:**

All liquid-in-glass field thermometers and thermistor thermometers should be calibration checked prior to each field effort. No mercury thermometers should be taken to the field. Networks are referred to Section 6.1.2 of the NFM (Appendix C-1) for specifics on recommended calibration procedures, check methods, and calibration intervals. All multiparameter sondes are equipped with thermistor thermometers, are calibrated by the manufacturer, and should be checked for accuracy against a NIST certified thermometer by Network technicians upon receipt from the manufacturer and at a minimum quarterly thereafter. The thermistors should be checked against a broad range of temperatures (e.g. from an ice water bath to beyond the range water body temperatures are expected to be encountered in the field; e.g. 45°C). If geothermal waters are being monitored, the instrument specifications should be checked against the anticipated temperatures for the geothermal waters.

If a temperature probe is found to not meet the temperature calibration requirements set forth in the NFM guidance, the entire multiparameter probe should be returned to the manufacturer for replacement. Once calibrated by the manufacturer, thermistor thermometers are one of the more accurate and stable sensors requiring the least maintenance. Multiparameter instruments are generally equipped with a thin-walled, titanium-sleeved thermistor that offers fast response and resists corrosion. The device is of high precision (e.g. 2252 ohms @ 25° C w/precision of  $\pm 1\%$ ) and uses an imbedded algorithm to convert resistance to temperature. When handled according to manufactures specifications, and checked on a regular basis, the sensor should provide a long period of useful operation. Radtke, Kurklin, and Wilde (1998) detail the proper calibration and documentation for thermometers and thermistor thermometers.

All temperature measurements should be made and reported in units of degrees Celsius (°C). Each Network lab should be equipped with a NIST certified digital calibration thermometer (preferred) or a liquid-in-glass thermometer graduated at 0.1 °C with a minimum range of -5 to + 45 °C. Prior to conducting fieldwork, temperature sensors used should be tested against thermometers certified by the National Institute of

Standards and Technology (NIST) for lab testing of temperature equipment. A second NIST certified digital thermometer may also be appropriate for field use and may best serve to field check the thermistor-based measurements of the multiprobes and measure ambient air temperatures when at the monitoring station. The USGS recommends that calibrations be performed at temperatures as close as possible to that of the environmental sample to achieve the highest accuracy. For this reason, calibrations are best performed in the field after calibration standards are brought into equilibrium (~15 min.) with the temperature of the water body to be measured (e.g. Hydrolab). However, YSI (with exception of DO calibration) and In-Situ indicate that calibrations performed with standards at 25° C or near room temperature are preferable.

#### **5.2.2.1.3 Measurement Methods and Accuracy**

Obtaining accurate field temperature measurements of ambient air and the adjacent water body should begin by examining the monitoring site for possible causes of temperature variation. Networks are directed to the methods and procedures outlined in the air and surface water temperature methods (Section 6.1.3 A, B, & C) in the NFM. When a thermistor thermometer is used in conjunction with a multiparameter probe, a cross-sectional profile of the water body may be generated from all parameters measured by the multiprobe during a single transect.

The measurement method and the resulting measurement recorded will be dependent upon the temperature variation exhibited by the cross-sectional profile, the sampling method selected, and the overall project or study objectives. Water conditions within a water body are of three general types that may require employment of different methods to obtain a representative parameter measurement. They include:

- Flowing, shallow stream (i.e. wadeable)
- Stream too deep or swift to wade (non-wadeable)
- Still water condition (non-flowing water body)

Network staff is directed to Section 6.1.3B of the NFM found in Appendix C-1 for detailed procedures to follow when dealing with these different water conditions. Recommended instrument specifications (range, resolution/sensitivity, and accuracy) for temperature measurements are found in Table C. 5-2.

Interferences to temperature measurements are specific to the device being used so the operator's manual should be consulted for this information. Temperature interferences are generally limited to the atmospheric temperature of the surroundings and the temperature of the device used to collect the sample. In-situ measurements of temperature generally minimize/avoid these common interferences.



#### 5.2.2.1.4 Reporting

All temperature measurements should be reported to the nearest 0.2°C when using a thermistor thermometer and to the nearest 0.5°C when using a liquid-in-liquid thermometer. Reporting temperature to the nearest 0.5 °C is generally acceptable (at a minimum) because temperature is usually somewhat variable across the water body. Field measurements of ambient air and computed mean or median water temperature should have entry blanks/positions on the standard field forms. Include the accuracy range of the instrument in the database as that reported in the manufactures specifications. If field conditions present obstacles that could have compromised making an accurate temperature measurement (or any other field parameter measurement), or caused the instrument to deviate from the reported instrument accuracy of the manufacturer, the technician should note this on the field form.

#### 5.2.2.1.5 Sensor Maintenance, Cleaning & Storage

Temperature instruments should be tested before each field effort and cleaned after each use. Ensure that the temperature extremes likely to be met in the field do not exceed the specifications of the instrument. There are various sources of guidance depending on the equipment used. For general guidance, refer to Section 6.1.1 and Table 6.1-1 of the NFM for equipment and supplies used to measure temperature. For specific guidance on multi-probes, this table should be supplemented by the equipment manufactures recommended supplies, maintenance, and cleaning procedures and solutions for the various temperature and other probes (e.g. see Hydrolab's Maintenance & Calibration Workshop Training Manual; YSI's Technical Guide for 6-Series Environmental Monitoring Systems or other appropriate guidance). The USGS has provided an excellent up-to-date guidance on temperature and other sensor based measurements used in continuous water quality monitors (Appendix C-3). The most recent version of this document may be downloaded from the web at <http://water.usgs.gov/pubs/wri/wri0042552/>. Continuous water quality monitors (multiparameter probes) typically employ thermistors that are reliable, accurate and durable sensors that require little maintenance and are relatively inexpensive.

#### 5.2.2.2 Specific Conductance (from Conductivity)

Conductivity or specific electrical conductance is a measure of the capacity of water (or other media) to conduct an electrical current. When the raw conductivity measurement of a substance is normalized to unit length and unit cross-section **at a specified temperature** (e.g. a compensation temperature of 25 °C), it is **specific conductance**. Specific conductance is dependent upon the types, quantities and ionic state(s) of dissolved substances. As concentrations of dissolved ions in water increase, specific conductance increases. Specific conductance is a good indication of total dissolved solids and total ion concentration. In addition to raw conductivity and specific

conductance, various other display options or approximate equivalents related to water's conductivity may be displayed or computed/derived from raw conductivity. These parameters and their commonly reported units include **salinity** (ppt), **TDS** (mg/l), and **resistivity** (milliohms), the inverse of conductivity. These parameter values depend on the instrument and the conversion algorithms provided with the instrument software or the conversion algorithm selected by the technician conducting the post-processing of the data. Conductivity values and related parameter measurements (specific conductance, TDS, salinity etc.) made on the same sample will thus differ somewhat between instruments due to the varying conversion algorithms and the specific design electronics of the equipment manufacturers. The accuracy of these built in conversion algorithms will also depend on the "type" of water measured, chemical species present, and the type of water (usually an ideal KCl, NaCl, or sea water equivalent solution) that the conversion algorithm is based upon. **For these reasons, the raw conductivity measurement must be recorded and reported along with any of the "derived" but preferred measurements (e.g. specific conductance for fresh waters and salinity for marine waters). Many data loggers and handheld displays offer the option of capturing and displaying two or more of these parameters simultaneously. However, instrument calibrations should be performed in the conductivity mode and most calibration standard solutions are reported in conductivity to avoid calibration variability or error inherent to various algorithms used to derive other conductivity-based parameters (specific conductance, salinity, TDS etc.).**

The electrical conductivity of a water body has little or no direct effect on aquatic life but because it is essentially due to the sum of all ionic species, its change (increase) may be detrimental if the particular ionic species or groups of ionic species (e.g. specific salts) causing the change is toxic to aquatic life. Conductivity often varies with flow and is therefore particularly important where flow is not quantitatively measured. Specific conductance can serve as a surrogate for total dissolved solids and is often best used as an early indicator parameter in baseline monitoring with more specific measurements of individual ions to determine cause and effect in follow-up sampling (MacDonald et al, 1991). The specific conductance (SC) and TDS relationship is very approximate (typically  $\text{TDS} \approx 0.6 \times \text{SC}$ ) due to the varying effects that species of differing ionic charge may have on conductivity and any presence of organic materials that do not carry electrical current. Some common sources of pollution that can affect specific conductance are deicing salts; dust reducing compounds, and mining operations. Salinity measurements are made in reference to a standard seawater (corrected to S= 35) at a temperature of 15 °C and a gauge pressure of zero.

#### 5.2.2.2.1 Measurement Theory

Conductivity measurements are based on the premise that when current (AC voltage) flows through two electrodes separated by an aqueous sample, the current level will have a direct relationship with the conductivity of the solution. Commonly a conductivity sensor/probe will consist of a cell (e.g.  $\text{cm}^3$  volume) with four (4) pure nickel electrodes. Two of the electrodes are current driven and two are used to measure the current drop caused by the conductivity of the intervening solution (water) being

measured. The **measured voltage drop is converted by a software algorithm into a conductance value and multiplied by the cell constant selected by the instruments software during calibration.** The cell constant may be selected automatically by the instrument during calibration and can thus vary with the ionic strength or conductivity of the calibration standard chosen. It is therefore important to **properly bracket your anticipated conductivities to be measured in some water body with the appropriate calibration standards.** This is done so that the appropriate cell constant will be used by the instrument's software to output the most representative specific conductance value. Some instruments are set up to apply a cell constant = 5.00 and are applicable to fresh, brackish and seawater.

The conductivity of solutions of ionic species is **highly dependent on temperature and may change as much as 3% for each 1°C change.** Thus a significant apparent change in conductivity may simply be a function of the water bodies (seasonal) temperature change. In addition, the temperature correction coefficient itself varies with the charge and abundance of the ionic species present (e.g.  $\text{Na}^+$  Vs  $\text{Ca}^{++}$ ) so no universally applied algorithm will be exact. A **raw conductivity value is not temperature compensated** making it difficult to compare measurements of the same or different water bodies when not at the same temperature (e.g. conducting trend analysis over time). For this reason, WRD requires reporting raw conductivity and temperature compensated (to 25°C) conductivity measurements or specific conductance (i.e. specific conductance = raw conductivity corrected to 25°C). This is also the convention used in national water quality programs such as NAWQA. In marine/estuarine monitoring, raw conductivity must also be measured and reported along with the derived salinity. Raw conductivity values may then be converted to both salinity (ppt) and specific conductivity by monitoring staff using standard algorithms for comparison to historical data or this will be done automatically by WRD at the time of uploading the data to STORET. **Because both specific conductance and salinity are “derived” parameters (from conductivity), raw conductivity should always be reported as well.**

Most multi-probes provide an option to output conductivity as specific conductance, salinity, TDS, or resistivity in addition to raw conductivity. Because there is no universal linear relationship between total dissolved substances and conductivity due to ionic activities and ionic charge differences of the dissolved species, the temperature compensated value of TDS that is derived from specific conductance can only be a close approximation. Specific conductance is based on an algorithm that is accurate for seawater and for solutions of many common salts such as KCl, NaCl and  $\text{NH}_4\text{Cl}$ . However, specific conductance is normally a very good surrogate to semi-quantitatively reflect a solution's dissolved solids and the gross change that may be occurring over time in that parameter. Similarly, the algorithms used to output TDS and salinity can only provide a close approximation to an actual analytical determination. It may also be possible to establish a more accurate relationship (algorithm) for converting specific conductance to TDS on a site- or water body-specific basis by comparing TDS from measured specific conductance with TDS lab determinations for a water body made at various flows/levels. One or more correction factors may then be derived for the

various flow conditions and their associated specific conductance to even more accurately approximate TDS.

Specific conductance measurements may be expected to differ slightly for the same solution when measured by instruments produced by different manufacturers if the same algorithms are not used in the software or the temperature measurements of each instrument are not identical. When different equipment or the equipment of different manufacturers is used to make conductivity measurements on the same water body/sub sample, it should be expected that these measurements will differ slightly. To understand such measurement differences between instruments (within the range of stabilization criteria) technicians should be aware of what algorithm is used in the particular instrument to compute specific conductance.

Algorithms which are applied automatically for the conversion of raw conductivity to specific conductance used by the USGS (NAWQA) and some vendor examples follow. Although the calculations most often result in only slight differences, they do explain why measurements by the manufacturers of different instruments should not be expected to read exactly the same for these “derived” values.

$$\text{Specific Conductance} = \frac{\text{Conductivity}}{1 + 0.019 * (T - 25)} \quad (\text{NFM, USGS})$$

OR

$$= \frac{\text{Conductivity}}{1 + 0.0181 * (T - 25)} \quad \text{TO} \quad = \frac{\text{Conductivity}}{1 + 0.020 * (T - 25)} \quad \begin{matrix} \text{(Various} \\ \text{Equipment} \\ \text{Vendors)} \end{matrix}$$

OR

$$= \frac{\text{Conductivity}}{1 + 0.0191 * (T - 25)} \quad (\text{Std. Methods 20}^{\text{th}} \text{ ed.})^*$$

**\* The algorithm from Standard Methods (20<sup>th</sup> ed.) is recommended for use by this guidance and will be the basis of any post-processing of conductivity data by WRD prior to STORET uploads.**

#### 5.2.2.2.2 Calibration and Units

Calibration of specific conductance is typically performed in the conductivity mode with standards expressed in conductivity at some temperature. Calibration should be done and the instrument checked before each field mobilization and an initial calibration at the start of each days activities prior to data collection. There are a variety of instrument types and manufacturers that produce conductivity cells and probes with differing operating procedures. Calibration of this equipment depends on instrument and

sensor type. Typically, the conductivity calibration involves the computation of a slope between two endpoints or known conductivity standards. Most instruments now have built in software that performs this two point slope-based calibration automatically. However, several instruments may provide for a one-point calibration. General conductivity guidelines are provided in Section 6.3.2 of the NFM. General guidance on calibration of continuous monitors (multi-parameter probes) that include a conductivity sensor are provided by Wagner et al (2001) @ <http://water.usgs.gov/pubs/wri/wri004252/> (Appendix C-3). This continuous monitoring document was last updated through Feb 2001 at the time of this writing. Radtke, Davis & Wilde (1998) provide detailed guidance on the calibration and documentation for specific conductance meters. To a large degree, these guidance's will apply generally to most conductivity instruments but network technicians should always calibrate the conductivity probe according to the specific instructions the manufacturer provides for that probe/sensor.

The USGS recommends that calibration of the conductivity sensor (and several others) of multiparameter probes be performed in the field with standards that have been allowed to equilibrate to the temperature of the water being monitored. This is also the recommended procedure of Hydrolab when their sondes are deployed (personal communication, Steve Combe, Electronic Data Solutions). However, some manufacturers recommend that the user calibrate specific conductance (conductivity and several other sensors) at temperatures as close to 25 °C as possible for best results (personal communication, Mike Lizotte, YSI; Glenn Carlson, In-Situ Inc.). The calibration is relatively straightforward.

Conductivity calibration standards are not buffered like pH standards so are highly susceptible to carry over of solutions of varying ionic strength or dissolved salt residue on the sensors when probes are not completely clean and dry. For this reason it is important to clean and dry the sensors (e.g. with chemwipes) between immersion in standards and a conductivity calibration standard should never be reused. Generally, the lower (ionic strength) the conductivity standard used, the greater the potential carryover error that may be introduced by its reuse through the dilution by DI water remaining on the probe/sensors or carry over of salts. Therefore, always calibrate from low to high (conductivity standard) and triple rinse sensor and calibration cup with the standard to reduce the possibility of solution carry-over.

#### 5.2.2.2.3 Measurement and Accuracy

It is recommended that **specific conductance** (freshwater) and **salinity** (marine/estuarine) measurements be made in-situ whenever possible to minimize the changes that are possible from the loss/gain of dissolved gases, solute precipitation, adsorption, ion exchange etc. that can occur when measurements are performed on a sub sample. The **raw conductivity** from which specific conductance and salinity is derived should also be recorded. Network technicians are directed to applicable state guidance and the procedures in Section 6.0 of the NFM and section 6.3.3 for detailed guidance on measuring surface water for conductivity in flowing or still water environments. Specific conductance measurements in flowing surface water should represent the cross-sectional

mean or median value at the time of observation (use Equal Discharge Increment or Equal Width Increment methods as appropriate). Deviations from this convention should be documented in the metadata.

Submersible multiparameter probes are generally best suited for in-situ measurements of specific conductance/salinity along with other sonde measurements that may be made concurrently. For larger, faster flowing, fresh water bodies or strong marine/estuarine current situations, the multi-parameter probe may be weighted to facilitate obtaining depth-integrated measurements or raised/lowered through screened metal, PVC or HDPE casing from a gaging station, bridge or cableway. Metal screens may affect some sondes so this should be determined in advance if deployment through metal piping is anticipated. The electrodes used to measure specific conductance are generally reliable, accurate, and durable but are susceptible to fouling from aquatic organisms and sediment when deployed in-situ for longer periods at continuous monitoring stations. Entrainment of air (bubbles etc.) in the conductivity cell during deployment is the most common cause of very low or erratic conductivity measurements. Entrainment of air is best avoided by ensuring that sondes break the plane of the water in a vertical position and are moved back and forth through the water column during initial deployment to remove any entrapped air.

Suggested accuracy specifications for specific conductance sensors are found in Table C. 5-1. Specific conductance and other water quality parameter calibration standards are available from several sources including YSI, Hydrolab, the USGS OCALA Water Quality Service Unit (WQSU), and through Calitech Standards & Supplies @[www.geoposition.com](http://www.geoposition.com) among others. Specific conductance standards now may be purchased in bulk at reasonable prices. These standards should definitely not be reused due to potential carry-over of solutions changing the specific conductance (unlike the minimal effects of tap or DI water carry over may pose for pH buffers). Calibration solutions also come with an expiration date that should be recorded in the instrument logbook along with other information when performing calibrations. Care should be taken in performing the proper conversion when calibration standards are labeled in units other than  $\mu\text{S}/\text{cm}$  ( $1 \mu\text{S}/\text{cm} = 1 \mu\text{mhos}/\text{cm}$ ), as the conversion to the appropriate units can be a common source of calibration error. Most calibration standards may be now prepared in a laboratory given the appropriate glassware, analytical balance sensitivity, analytical grade chemicals, and safety equipment/procedures. Some chemicals and prepared standards can be toxic/carcinogenic (e.g. formazin turbidity standard), so should be handled with extreme care.

Temperature, ionic strength and selection of the cell constant are features that affect the measurement of conductivity. Significant error (2 to 3 percent per  $^{\circ}\text{C}$ ) may occur if in the temperature compensated measurement of conductivity (specific conductance), the temperature measurement is inaccurate. Conductivity of a solution is also a function of the concentration and charge of the ions in solution and the rate at which ions move under the influence of an electrical potential. As the ionic strength increases, the rate at which the individual ion will move, decreases. A linear relationship exists for specific conductance and ionic strength for solutions below  $1,000 \mu\text{S}/\text{cm}$ . As

specific conductance increases above 5,000  $\mu\text{S}/\text{cm}$ , the line slope changes significantly; beyond 50,000  $\mu\text{S}/\text{cm}$ , the specific conductance is an unsatisfactory index of ionic concentration.

The cell constant used in specific conductance measurements should be checked and verified on a regular basis and the appropriate cell constant selected for use in marine or freshwater monitoring. A significant change in the cell constant indicates that the electrode needs cleaning or changing. For many multiparameter instruments, verification of the cell constant is performed during calibration and is a preferred means of quality control.

#### 5.2.2.2.4 Reporting

Specific conductance is the required measurement Servicewide for reporting conductivity (freshwater) although the raw conductivity measurement should always accompany the specific conductance. Both measurements should be reported in units of  $\mu\text{S}/\text{cm}$  (microsiemens/cm = micromhos/cm), with specific conductance normalized (usually automatically) to 25°C (i.e. the temperature compensated value in microsiemens per centimeter). This will facilitate Servicewide comparison of data and trend analysis of the monitored fresh water bodies.

For the marine/estuarine system, conductivity (and specific conductance if desired) may be reported in  $\text{mS}/\text{cm}$  and then converted to salinity using the algorithm in Standard Methods (ALPA1998) or preferably, the JavaScript calculators using the UNESCO International Equation of State (IES 80) found at: <http://ioc.unesco.org/oceanteacher/resourcekit/M3/Converters/SeaWaterEquationOfState/Sea%20Water%20Equation%20of%20State%20Calculator.htm>). However, salinity is also computed automatically by multi-parameter instruments with the appropriate built in conversion algorithm. Salinity is normalized to 15° C and determinations are based on the Practical Salinity Scale of 1978 where conductivity of a KCl solution containing a mass of 32.4356 grams in a mass of 1 kg of solution is defined as having a practical salinity of 35. The conductivity of such a solution should be 42.914  $\text{mS}/\text{cm}$  with a density of 1.025  $\text{gm}/\text{cc}$  at zero gauge (1 atm.) pressure.

Modern freshwater monitoring systems are designed for medium strength specific conductance waters (100 to 2,000  $\mu\text{S}/\text{cm}$  or 0.1 to 2.0 millisiemens/cm). Computations of salinity are generally not made for freshwater. Consult with the instrument manufacturer/operations manual to ensure that the cell constant for the conductivity sensor is appropriate for the ionic strength of the anticipated waters. Monitoring staff should indicate the desired range of use for the conductivity sensor to the manufacturer prior to procurement of the instrument to avoid measurement errors from using a cell with an inappropriate cell constant.

The following information about field measurements of specific conductance shall be logged (manually or electronically) and reported for quality-assurance documentation.

Calibration Standards used – source and expiration dates  
 Instrument manufacturer and model  
 Date and time of calibration check  
 Temperature and conductivity of standard used in calibration check  
 Sample temperature, conductivity and specific conductance measurement  
 Name of person(s) performing the calibration and measurement

#### **5.2.2.2.5 Sensor Maintenance, Cleaning & Storage**

As with other sensors, the specific conductance/conductivity sensor should undergo periodic inspection and operational testing at the Network lab/office to ensure the equipment is in good operating condition. Maintenance functions tend to be vendor/sensor specific but commonly include removal of the cell block and o-rings to expose the nickel electrodes so corrosion may be removed with an abrasive paper. Normally, short-term storage (days to a couple weeks) of the conductivity cell/probe along with other sensors attached to the multi-parameter probe is acceptable in a very moist/water saturated air environment. This is accomplished by maintaining a piece of saturated sponge or small amount of tap water in a cup partially covering (~1/8) the sensor that is supplied with the instrument.

For longer-term storage (2 weeks or more), it is generally better to remove all sensors from the sonde/multi-probe and store them per the manufacturers specific instructions. All instrument manuals provide maintenance, cleaning, and storage instructions that should be consulted for important instrument-specific directions on these subjects. More complete storage information and storage “tips” are generally available by speaking with manufacturers technical support via their 1-800 number or consulting the instrument operation manual. Storage in areas away from dust, excessive heat and cold is also important in extending the life of the sensor. Cable connectors should be kept dry, free of dirt and extraneous matter and protected in a clean plastic bag when not in use.

It should be standard procedure to clean sensors thoroughly with deionized water before and after making a measurement. Any oily residues or salts should be removed from sensors by soaking in a weak detergent (e.g. alconox) solution. Soaking conductivity electrodes (only) with persistent residue for a minute or less in dilute hydrochloric acid may be acceptable but the manufacturer’s recommendations to resolve residue problems should be consulted first. The dilute hydrochloric acid treatment generally works well and a little goes a long way (personal communication, Bob Boulger, USGS).

#### **5.2.2.2.6 Other Display/Readout Options**

Additional display options for the specific conductance and raw conductivity measurements ( $\mu\text{S}/\text{cm}$ ,  $\mu\text{mhos}/\text{cm}$ , or  $\text{mS}/\text{cm}$ ) may include , salinity (ppt), and total dissolved solids (TDS) in  $\text{mg}/\text{L}$  when there is another immediate use for any one of these



measurements in monitoring. However, in freshwater monitoring, at a minimum conductivity and specific conductance shall be reported to WRD for uploading into STORET. In marine/brackish water conditions, raw conductivity, and salinity should be reported. All other conductivity parameters that may be derived from specific conductance (e.g. TDS, resistivity) using a standard algorithms from the more recent versions of Standard Methods (e.g. 20<sup>th</sup> ed) may be reported at the discretion of the Networks. In newer multi-parameter sondes, salinity is automatically calculated from conductivity and temperature. Salinity is also used to compensate the DO measurement for the “**salting out**” effects that higher dissolved solids have on DO above 1800 to 2000 mg/L.

In general, a range of 0 to 70 ppt., an accuracy of +/- 1.0% of reading or 0.1 ppt. (whichever is greater), and a resolution/sensitivity of 0.01 ppt. is a typical performance specification (YSI Series 6 Technical Guide) for the salinity measurement. However, individual manufacturer’s instrument specifications should be consulted for applicable performance specifications and only recently has the Practical Salinity Scale been extended to low salinities using a single algorithm that is valid from 0 to 40 salinity (Standard Methods, 1998; 20<sup>th</sup> ed.).

Total dissolved solids may also be very approximately determined from conductivity measurements by the relationship  $KA = S$ , where K is the conductance in  $\mu\text{S}/\text{cm}$  (or micromhos), S is the dissolved solids in milligrams per liter, and “A” is the conversion factor. “A” can vary from 0.54 to 0.96 but usually falls between 0.55 and 0.75, the higher values generally being associated with waters high in sulfate concentration (Hem, 1985). Each multi-probe manufacturer that provides a TDS output has selected a conversion factor (commonly 0.6 is used for A) used in the instrument software to convert raw conductivity to TDS. Each Network should verify with the instrument vendors what various algorithms are being used to obtain the derived values for specific conductance, salinity and TDS to ensure the appropriate algorithm is used. In general, those algorithms found in recent editions of Standard Methods (APHA, 1998) are preferred in the Vital Signs program unless unusual environmental waters are encountered.

### 5.2.2.3 pH

The term pH is derived from “p” meaning power and “H” for the element hydrogen and literally means “**power of hydrogen**”. The importance of pH as a parameter for monitoring is reflected by potential impacts to the life cycle stages of aquatic macroinvertebrates and certain salmonids that can be **adversely affected when pH levels above 9.0 or below 6.5 occur**. Metals mobility is also enhanced by low pH with **arsenic** an exception being mobilized at higher pH. Thus, pH can play a significant factor in impacts to water bodies located in areas contaminated by heavy metals (e.g. mining). Estimating/computing the toxicity of ammonia, aluminum, and some other contaminants requires accurate pH values as metadata. Temporal causes of variation of pH can range from primary production by fauna and flora (diurnal and seasonal) to

fractionation during snowmelt, changes in runoff processes, and changes in atmospheric deposition (monthly and/or seasonal) (MacDonald et. al., 1991).

pH is measured to determine the acid/base characteristics of water and is controlled by interrelated chemical reactions that produce or consume hydrogen ions (Hem, 1985). It is defined as the hydrogen ion concentration in moles per liter ( $\text{Moles L}^{-1}$ ) and is represented as the negative log (base 10) of the hydrogen ion concentration ( $-\log [\text{H}^+]$ ), although in effect it is the activity of hydrogen ions and not their actual concentration that determines pH. The pH scale can range over 14 orders of magnitude although extremely acid pH (negative) of natural waters has been reported at Iron Mountain Mine, CA (personal communication, Roy Irwin, WRD). Natural waters can fall in the range of 0 (highly acidic) to 14 (highly basic) but most commonly fall in the range of 4 to 9, with their pH a function of the relative activities of  $\text{H}^+$  and  $\text{OH}^-$  ions they contain. Generally, dissolution of carbon dioxide is the most important buffering system (carbonate system) in extremely fresh natural waters to affect pH ( $\sim$  pH of 6) in the absence of some other site-specific conditions. However, most natural waters are slightly basic ( $\sim$  pH of 8) due to the presence of carbonates ( $\text{CO}_3^{2-}$ ) and bicarbonates ( $\text{HCO}_3^-$ ).

#### 5.2.2.3.1 Measurement Theory

The measurement of pH requires a sensing electrode for  $\text{H}^+$ , a reference electrode, a meter to measure the electrode potential, and buffers to calibrate the system. A glass sensing bulb is filled with solution of stable pH (usually 7) so the inside of the glass experiences a constant binding of  $\text{H}^+$  ions. The outside of the glass bulb is exposed to sample where  $\text{H}^+$  varies (from sample to sample). The differential in hydrogen ions across the glass boundary separating the sample from the solution inside the bulb creates a potential that is read versus the stable potential of the reference electrode. This potential, measured in millivolts (mv), is related to the pH by a form of the Nernst Equation. The plot of the pH versus voltage is linear and is used to convert the voltage to pH. The slope of the pH vs. potential (mv) plot at temperatures different from calibration can also be determined from an equation (YSI, Technical Guidance).

For natural waters of low ionic strength (i.e. weakly buffered at near neutral pH), the pH measurement may appear unstable (bounce between several tenths of pH units) because the differential in hydrogen ions across the glass bulb cannot be maintained constantly by the sample. Under such conditions, reaching stabilization of the pH measurement can require up to 20 minutes after calibration and conditioning the sensor in a low ionic strength solution prior to deployment may help. Alternatively solving the problem may require calculation of a mean or median value. Some multiprobe vendors offer an optional low ionic strength reference electrode to facilitate pH measurements in low ionic strength surface waters.

#### 5.2.2.3.2 Calibration and Units

The pH instrument should be checked and calibrated prior to field mobilization and upon arrival at the site before initiating sampling. In general, WRD recommends following the pH calibration procedures outlined in the NFM and followed by NAWQA subject to modification by any manufacturers guidance for the particular pH sensor employed. Calibration of pH instruments/sensors related to low-conductivity waters ( $< 100 \mu\text{S/cm}$ ) are also provided by this source (NFM, 1998). Radtke, Busenberg and others (1998) describe the calibration of pH meters in a ten-step process that is generally applicable to a wide range of instruments. **Calibration of pH probes in multi-parameter sensor systems are best performed by following the manufacturer's specific instructions laid out in the operations manual.**

Because pH is temperature dependent (i.e. hydrogen ion activity varies with temperature), the pH of buffer solutions must be known and temperature correction factors applied during calibration of some older model equipment. Two buffers should be selected which bracket the anticipated pH of the water body to be sampled with a third buffer selected to check instrument performance over an extended range. In most monitoring situations, buffers of pH 4, 7, and 10 will suffice but other buffers should be available when waters are encountered that fall outside this range. The normal procedure is to establish the null point with the pH 7 buffer and then determine the slope of the calibration line with the second buffer (pH 4 or 10) that brackets the anticipated pH of the water body. The USGS indicates this calibration should be done as close to the temperature of the water body as possible (NFM, 1998) but this requirement may not be required with some vendor's newer equipment. Immersing the buffer solutions in the water body for approximately 15 minutes will normally allow them to equilibrate to the proper temperature for this calibration. In-situations where field alkalinity is determined, calibration of the pH meter should include three (3) buffers.

The more modern instruments are equipped with microprocessors that perform autocalibration operations that automatically compensate for buffer temperatures by deriving the Nernst slope. This permits skipping several of the calibrations steps necessary for older instruments (NFM, 1998). The response and Nernst slope of the pH electrode should be checked upon purchase of the equipment and at regular intervals thereafter. Optimum electrode response is characterized by a slope of from 98 to 99.5 percent with a slope of 94 percent indicating possible electrode deterioration and a 90 percent slope cause for electrode replacement.

#### 5.2.2.3.3 Measurement and Accuracy

In-situ measurement of pH is recommended for surface waters because the pH of a water sample can change significantly within minutes as a result of degassing, precipitation, or temperature change etc.. The electrometric method of pH measurement employs combination electrodes consisting of the proton selective glass bulb reservoir filled with a pH 7 buffer and a Ag/AgCl reference electrode. This is the most common technology and should be the standard measurement method. The colorimetric (litmus)

method is only suitable when rough estimates of pH are needed such as determining if adequate preservative has been added to samples for lab analysis. This latter method is also subject to interference from turbidity, color, colloidal matter, and oxidants etc. However, the litmus test method can serve as a quick check when instrument measurements appear anomalous.

Detailed guidance of field pH measurements using combination electrode based instruments is provided in the NAWQA NFM. Radtke, Bausenberg and others (1998) and Busenberg and Plummer (1987) describe calibration and proper measurement techniques for low specific conductance waters less than 100  $\mu\text{S}/\text{cm}$ . Networks that deal regularly with these types of water should consult these sources for further guidance as pH measurements under low water conductivity conditions can be problematic. Optional low ionic strength reference electrodes are available to facilitate accurate pH measurements in waters of low ionic strength (Hydrolab, 2000).

The pH measurement is relatively free from interferences due to color, turbidity, colloidal matter, oxidants, or reductants. Temperature, atmospheric contamination and ionic strength are factors that affect the pH measurement. Dissolved oxygen and carbon dioxide can be evolved or dissolved when the sample is exposed to air and a considerable change in pH may result. pH measurement error due to a sample's ionic strength are relatively small for most natural waters and are generally not corrected in the field. pH measurements are accompanied by measurement of specific conductance so that some qualitative assessment may be made as to how the hydrogen ion activity may be affected by other dissolved ionic species. High sodium ( $> 10$  moles/L) and high alkalinity (when  $\text{pH} > 9$ ) of a sample may also produce pH measurement errors and require a special electrode. Also, for sample pH's less than 1 or greater than 9, the measurement will have greater uncertainty because the electrode response is non-Nernstian in these regions.

#### **5.2.2.3.4 Reporting**

Reporting of all pH measurements should be in pH units as that is the standard unit of measurement for pH. Measurements of pH should be reported to nearest 0.1 standard pH unit for data entry. Instrument accuracy and precision should be reported as that provided by the manufacturer in the instrument specifications. Accuracy and precision of field measurements will usually be something less than that of the instrument sensitivity/resolution (typically 0.01 pH units) due to variables introduced by field conditions. This latter precision and accuracy cannot be quantified but should approach that of the instrument provided good field protocols are followed. pH data is necessarily recorded electronically by multiparameter probes at continuous monitoring stations due to the high frequency and large number of measurements made. For intermittent monitoring (stations), pH data may be recorded manually. However measurement of pH by multiparameter instruments allow for large data records to be generated, even when conducting intermittent manual water quality sampling. Networks are therefore recommended to implement electronic methods of data capture whenever possible when collecting and recording water quality parameter measurements.

### 5.2.2.3.5 Sensor Maintenance, Cleaning & Storage

Busenberg and Plummer (1987) recommend monitoring the slope and measured potential of a new pH electrode for a period of one week before use. This has become relatively easy with new instruments that contain microprocessors that automatically calculate and display the slope. The equipment operator should determine the new electrodes drift and percent slope during this period and ensure that the slope stabilizes to within  $\pm 0.2$  percent of the Nernst slope after the electrode has been conditioned by following the procedures recommended by the manufacturer. Should the electrode fail to stabilize within this range, the equipment vendor should be contacted for possible sensor replacement.

The first source or guidance consulted for pH sensor maintenance, cleaning and storage should be that of the manufacturer. Maintenance of pH electrodes can sometimes be quite significant, particularly if subject to continuous or regular use and exposure to waters of poor quality. The reference electrode is either gel-filled (non-refillable) or liquid filled (i.e. may be reconditioned) with the former requiring the least maintenance. The liquid-filled electrode may be reconditioned or refilled several times, provides for longer life, and is potentially of less expense in replacement cost, as deterioration of these electrodes is normal. Network technicians should consult the NFM for the eight (8) basic steps that should be followed in pH electrode maintenance to facilitate years of reliable service. Procedures for reconditioning liquid-filled electrodes are also provided there.

Recommended storage procedures for pH electrodes vary with length of time, and electrode type (gel or liquid filled). Storage procedures can also sometimes vary with manufacturer. Shorter-term (days to a few weeks) storage methods are appropriate for electrodes in regular service or when moving between monitoring sites. The manufacturer normally recommends the best storage method and storage solution for the particular pH electrode type. Storage solutions can have a limited shelf life. Generally, storing glass hydrogen electrodes in deionized water or concentrated KCl solutions should be avoided. Water with some ionic strength (e.g. tap water) is preferred for shorter-term storage because deionized water may cause some sensors (e.g. KCl in reference electrode) to weaken as ion transfer occurs across cell membranes due to the concentration gradient. Therefore, **storage in DI water should generally be avoided.** Liquid-filled pH electrodes should be stored upright and kept wet (immersed). Gel-filled electrodes must only soak in a solution (sample) for a short time during measurement and therefore may not be appropriate for use in continuous monitoring situations (consult manufacturer).

Longer-term storage of electrodes requires that they first be cleaned (outer surface) with deionized water and in the case of liquid filled electrodes, be drained and stored dry. The manufacturer should be consulted to determine if the bulb should be kept moist. The storage area should be clean, dry and protected from hot or cold temperatures.

#### 5.2.2.4 Dissolved Oxygen (DO)

Dissolved oxygen (DO) is important to measure in surface water because the parameter is affected by numerous natural phenomena and human activities. DO is necessary in aquatic systems for the survival and growth of many aquatic organisms. The presence and amount of dissolved oxygen in surface water also determines the extent to which many chemical and biological reactions will occur (NFM, 1998).

Principal sources of dissolved oxygen in surface waters include **dissolution of atmospheric oxygen** in water as oxygen is depleted (re-aeration) and **photosynthetic activities of aquatic plants**. The primary sinks or consumptive users of DO include **respiration** and **biochemical oxygen demand (BOD)**. As a general rule of thumb, DO maxima and minima in the course of a diurnal cycle occur in early afternoon and early morning (just before sunrise), respectively. Because oxygen is sparingly soluble, the balance between sources and sinks can be sometimes easily upset leading to oxygen extremes of supersaturation or total/near total depletion. Oxygen is more soluble in cold water than warm and is prone to supersaturation in turbulent or highly productive water bodies.

Low dissolved oxygen is of greatest concern due to detrimental affects on aquatic life. Conditions that generally contribute to low DO levels include warm temperatures, low flows, water stagnation and shallow gradients (streams), organic matter inputs, and high respiration rates (MacDonald, 1991). DO concentrations in surface waters are typically in the range from 2 to 10 milligrams per liter (mg/L) although most aquatic life requires average DO levels of at least 5 mg/L to survive.

##### 5.2.2.4.1 Measurement Theory

Field methods for determining dissolved oxygen in water include the amperometric method and the spectrophotometric method. A third method (iodometric) involves titration (Winkler) and is generally not recommended for field determination of DO. The **amperometric method** is the standard procedure by which DO is determined in the field using a probe and is recommended in this guidance. The method requires the use of a temperature compensating instrument or meter that works with a **polarographic membrane-type or pulsed-type sensor**. The galvanic DO sensor is a third type rarely used in field applications until deployed recently by Horiba (U-20 series probes). Each sensor has its own theory of operation and specific benefits with the **Clark polarographic DO sensor** being the most common and discussed below.

The Clark polarographic DO sensor consists of a gold cathode and silver anode in KCl solution, and typically a 1 mil thick Teflon membrane. A voltage (0.8 volts) is applied to the cathode/anode causing all oxygen to be consumed in the KCl at the cathode. Depletion of the DO in the KCl solution causes diffusion of DO ( $O_2$  molecule) to occur across the Teflon membrane from the sample to the KCl solution and on toward the cathode. After a few minutes the electrochemical reactions occurring at the anode and cathode reach a steady state and generate a potential directly related to the diffusion

rate of molecular oxygen across the Teflon membrane. Because the diffusion rate is a function of the concentration of DO in the sample, the DO may be determined by the voltage output generated by the sensor. This method **depletes oxygen in the sample at the membrane boundary so fluid movement (stirring) of the sample must be maintained to ensure fresh sample water flows past the membrane and the DO gradient remains constant.** Hydrolab and In-Situ employs the Clark polarographic DO sensor technology. To avoid O<sub>2</sub> depletion at the sensor membrane, these vendors use a mechanical stirrer to maintain a minimum ( $\geq 1$  ft./sec.) water flow past the membrane.

The **rapid pulse DO sensor** employed by YSI also uses the Clark polarographic technology but pulses the 0.8 voltage applied to the cathode and anode. The rapid pulse technology does not require a steady state DO diffusion to be established across the Teflon membrane but instead determines the diffusion gradient resulting from this series of short electrical input pulses. Stirring or water movement past the membrane is not required with this technology to obtain accurate DO measurements.

#### 5.2.2.4.2 Calibration and Units

Calibration of the DO sensor can be one of the more involved calibrations to undertake due to corrections for temperature, barometric pressure/altitude and specific conductance (salinity) in instances where that parameter exceeds 2,000  $\mu\text{S}/\text{cm}$ . Use of multiparameter instruments that automatically compensate for one or more of these environmental conditions has simplified the calibration process somewhat, but an underlying understanding of how the equipment operates and how these environmental variables affect the instruments operation remains crucial. The DO instrument or DO sensor of the multiparameter probe should be checked and calibrated prior to field mobilization and a field calibration performed as close as possible to the temperature of the water body upon arrival at each monitoring station. This is often best achieved by **conducting the DO calibration with the multiprobe wrapped in a wet towel (white) that has been soaked in the water body** (personal communication, Mike Lizotte, YSI).

The USGS NFM (Table 6.2-1) provides a list of recommended equipment and supplies used in field determination of dissolved oxygen that Network staff should consult and modify to meet the specific needs of the field effort and the specific DO sensor or instrument type. Because calibration and operation procedures can differ significantly among instrument types and makes, the manufacturer's instruction/operation manual should be the principal source of calibration guidance. The Network technician should have a high level of familiarity with the DO instrument/sensor and its calibration prior to performing field measurements. Of the core parameters, DO remains the most problematic and prone to failure and erratic or false out of range measurements. Because a one point calibration of the sensor is performed at saturation (water-saturated air), WRD recommends that a **low DO solution** of anhydrous sodium sulfite (~ 4.4 grams) and cobaltous chloride (0.05 grams) dissolved in one gallon of distilled water (w/ little or no headspace) be prepared for field check purposes (see field measurement tips in Appendix C-7).

The NFM discusses 4 different methods that may be followed for DO calibration. They include (1) air calibration chamber in water **(2) water-saturated air calibration chamber** (3) air calibration chamber in air and (4) idiometric (Winkler) titration. Method # 4 is generally the most accurate but not as practical for the broader applications and conditions of the field. Calibrations performed in the field are now most often performed in water saturated air (i.e. water saturated air chamber or calibration cup) or some variant of method #1 (e.g. instrument wrapped in a white wet towel) based on the instrument manufacturers calibration guidance. The **water-saturated air calibration** method or procedure is recommended in this guidance as most of the newer sensors (YSI and Hydrolab) are calibrated more easily and relatively quickly in the field and with acceptable accuracy using saturated air calibration methods. Detailed information on the proper calibration and documentation of DO instruments or meters are detailed by Radtke, White, and others (1998) as well as the various instrument-specific calibration and operation manuals supplied by the manufacturers of DO probes.

The calibration of the DO meter in water-saturated air is a 1-point calibration performed in the % saturation mode (not mg/L). The method is discussed as it relates to the use of multiparameter sondes by Wagner et al (2000). The calibration is made at 100-percent oxygen saturation by adjusting the meter reading for air saturated with water vapor to a value obtained from a solubility table generated from the equations of Weiss (1970) and listed in Radtke, White, and others (1998) (now done automatically by most sondes). The 100 percent saturation value is based on the water temperature and the **uncorrected (to sea level) or true barometric pressure**. A **pocket altimeter or a barometer built into the hand held displays of newer instruments** that measures true barometric pressure to the nearest 1 mm of mercury (uncorrected to sea level) should be used at the monitoring station in this calibration procedure.

A **sodium sulfite reference solution** (oxygen scavenging) or other zero/near zero DO solution may be prepared and used to verify the accuracy of the DO instrument measurement near 0 mg/L dissolved oxygen. **Use caution** (gloves and eye protection) in handling these chemicals as they are toxic in concentrated form. The calibrated accuracy of DO meters using the saturated air calibration method should be within the lesser of 5 percent of the measurement range or  $\pm 0.3$  mg/L. Zero DO sodium sulfite solutions should measure less than 0.2 mg/L DO or the instrument should be recalibrated or checked for malfunction. Stability of the low DO solution should be at least 1 week depending on storage conditions and container headspace (headspace should be kept as minimal as possible and solution may be returned to container after DO measurement checks).

DO membrane electrodes are sensitive to temperature as the **diffusion rate of DO across the membrane will vary with temperature**. Automatic temperature compensators in most of the newer instruments correct for temperature variation. Higher salinities also impart an upward bias to the DO measurement and these should be corrected manually above 1800 to 2000 uS/cm specific conductance if not done automatically by the instrument. Oxygen-permeable membranes are also permeable to **chlorine and hydrogen sulfide** gases. These **gases can desensitize the DO probe**



during longer-term exposure. Such conditions sometimes may be found in stagnant or stratified waters adjacent to lake-bottom sediments. Because atmospheric oxygen is rapidly absorbed by water samples, **in-situ measurements are preferred.**

#### 5.2.2.4.3 Measurement Methods and Accuracy

This guidance provides for the measurement of dissolved oxygen in-situ only. Dissolved oxygen measurements made on subsamples is inaccurate due to the rapid changes that can take place in DO levels from affects of sample splitting or separation from the water body. When making a dissolved oxygen measurement in-situ, the technician should still be aware of what effects variables such as temperature, barometric pressure, and dissolved-solids have on the solubility of oxygen. **Higher absolute concentrations of dissolved oxygen (mg/L)** at saturation are achievable in the natural environment under conditions of **higher atmospheric pressure and lower temperature and lower dissolved solids** content of the water. Thus, water bodies occurring at higher elevations, subject to a barometric low pressure system, or having warmer temperatures and/or higher dissolved solids content would be expected to contain less dissolved oxygen at saturation. Supersaturation of surface water with respect to dissolved oxygen may also result from turbulence associated with high gradient streams or waterfalls and photosynthetic activity of plants.

The standard DO determination most representative for surface water should be a cross-sectional mean or median concentration of the dissolved oxygen at the time of observation (NFM, 1998). Dissolved oxygen is normally measured at a distinct spot and is considered representative of a flowing water body only when the DO cross-section variation is determined to be less than 0.5 mg/L (e.g., under ideal mixing conditions in a stream). In such instances, measurement of DO in a single vertical at the centroid of flow provides a representative value. Under these conditions, continuous monitoring stations may be most applicable. USGS NAWQA protocols prescribe that DO measurements in streams should not be made:

- (1) directly below sections with turbulent flow
- (2) in still water or
- (3) from/immediately adjacent to the bank

unless these conditions represent most of the reach or are required by the study objectives. WRD recommends that this guidance be adhered to as much as possible and if deviated from, be documented in the metadata. When in-situ DO measurements cannot be made, measurement of DO by meter in a bucket or using a **Winkler titration (iodometric titration) backup kit** is recommended.

Dissolved oxygen sampling for Aquatic Life use standards compliance under the CWA targets water bodies where previous low instantaneous D.O. levels indicate partial or nonsupport of designated aquatic life uses. When possible, intensive or continuous monitoring is conducted with automated sondes preset to record and store field measurements at hourly or less time increments. Alternatively, measurements may be

made manually at 4 to 6 hour intervals over a 24 hr period, provided a measurement is made near sunrise (typically the D.O. minima in a diurnal cycle falls between 0500 and 0900 hrs). The 24-hr average D.O. value is then reported as a time composite sample

Under conditions where measured specific conductance exceeds 2,000  $\mu\text{S}/\text{cm}$  and when using a sonde that does not automatically correct DO measurements for salinity, a salinity correction should be applied to the dissolved oxygen measurement. A correction is necessary due to the “salting out effect” of the polarographic oxygen probe that dissolved solids exert (slightly high bias) in making the DO measurement. A table of these correction factors and discussion of how they should be applied is found in Section 6.2.4 of the NFM. However many multi-parameter instruments have built in corrections for salinity effects on D.O.. The DO may also be corrected using a correction factor computed from the formula below:

$$F = 1 - \left[ 0.003439 + \frac{0.361}{(22.1 + T)^2} \right] \frac{C}{1000}$$

Where:

F = the adjustment factor

T = water temperature in  $^{\circ}\text{C}$

C = specific conductance ( $\mu\text{S}/\text{cm}$ )

Then:

$$\text{corrected D.O.} = \text{field D.O. value} \times F$$

Obtaining accurate DO measurements under a variety of surface water conditions (flowing shallow streams, streams to deep or swift to wade, and still-water) require application of methods appropriate for those conditions. Section 6.2.2.C of USGS NAWQA protocols (NFM) provide 7 steps that should generally be followed to facilitate DO measurements under these variable surface water conditions. Potential sources of measurement error to consider when following these steps include:

1. too low a velocity ( $< 1 \text{ ft./sec}$ ) can deplete DO at the sensor membrane boundary resulting in an erroneously low DO reading
2. too high a water velocity or turbulence can cause a streaming effect at the sensor membrane boundary and result in an erroneously low DO reading
3. not allowing enough time for DO measurement to stabilize

Solutions to problem #1 include adding an automatic stirrer, manually moving the probe through the water (up and down) or using an instrument with the rapid pulse DO technology (no stirring required). Solutions to problem #2 range from finding another cross-section profile location to inserting the sonde in a section of screened pipe to reduce water velocity past the sensor. Problem #3 may be solved by added **technician patience**.

The several variables involved in dissolved oxygen measurements increases the number of possible solutions when troubleshooting. Table 6.2-4 of the NFM provides a

troubleshooting guide. That table, along with any troubleshooting guidance provided by the manufacture are good places to start when resolving operational problems. Generally, operational experience and advancement up the learning curve gained through problem solving under a variety of field conditions is usually the best aid in identifying and resolving instrument problems.

The measurement of DO when concentrations occur in surface water less than 1 mg/L (suboxic water bodies) may require use of the spectrophotometric method. The technique has a sensitivity of 0.006 mg/L and is based on the Rhodazine-D™ colorimetric technique. This method should be considered when greater sensitivity in DO measurements are required in measuring suboxic conditions or if the DO sensor being used does not output within 0.2 mg/L of the 0.0 mg/L actual DO level when checked against the low range (suboxic) reference DO solution ( sodium sulfite and cobaltous chloride solution described earlier). When operating in a regulatory context, State DO measurement protocols should be consulted to ensure monitoring methods will be acceptable and documented with sufficient metadata.

#### **5.2.2.4.4 Reporting**

Measurements should be reported to the nearest 0.1 mg/L for amperometrically (probe/sensor) determined DO values that fall within the range of 0.1 to 20 mg/L. Under some conditions of extreme supersaturation, DO measurements may exceed 20 mg/L. In such situations and where DO values are exceedingly low (< 0.1 mg/L), WRD recommends defaulting to the NAWQA protocol and simply reporting these results as > 20 mg/L and 0.0 mg/L, respectively. The accuracy range and precision of the instrument specified/published by the manufacturer and that of the method (if possible) should also be reported (see table C. 5-1 for recommended examples). Field forms should be filled out completely, indicating the method used and sufficient metadata to support STORET requirements.

Meta data requirements to ensure QA documentation is sufficient for the field DO measurement include:

1. Date and time of calibration
2. Date and time of last zero check
3. Atmospheric/barometric pressure and altitude of site
4. Temperature (air) of calibration (for saturated air calibration method)
5. Calibration value
6. Sample temperature
7. Instrument manufacturer and model number
8. Name of person performing measurement

It should be noted that Hydrolab and YSI dissolved oxygen sensors should measure the same or nearly the same DO value in mg/L but not the same % saturation. This is because the Hydrolab % DO saturation is based on the 100% saturation value relative to sea level and YSI's % saturation measurement is based

on the 100% saturation value for the altitude of the site. Therefore, reporting of DO in per cent saturation is optional and should always include the brand of meter used.

#### 5.2.2.4.5 Sensor Maintenance, Cleaning and Storage

WRD recommends that the specific manufacturer's guidance for maintenance, cleaning and storage be followed for sophisticated electronic equipment of the type used in dissolved oxygen measurements or multiparameter sondes in general. These instruments require reasonable care in handling and operation. The manufacturer's guidance should be specifically followed for both short-term (field) and long-term (office) storage of sensors and for performance checks. This includes care taken during transport of instruments to avoid them being jostled or subjected to sudden impacts, rapid temperature changes, or extremes of heat and cold. For multiparameter instruments in particular, transport to the field/between monitoring stations within a single large pelican case equipped with cutout foam padding to surround and protect the instruments generally provides good protection. Newer cases (YSI) are airtight and watertight and come equipped with an E-Z purge valve/knob to control pressure. Sensor membranes are then subjected to a controlled equalization of pressure between sites of different altitude or when air transporting the sonde. Under extremely cold field conditions a pre-packaged chemical warmer (hand/foot) may be placed in the transport case to keep sensors from freezing during transport and prior to deployment. Removing the sensors from the probe and carrying them in an inside pocket is another option to prevent them freezing during any backcountry winter monitoring. **Shortening of battery life under very cold conditions** for both the display and the sonde is also a consideration that may need to be addressed for backcountry monitoring.

Before each field mobilization to perform DO measurements, a variety of performance checks should be run on the various DO instrument components and accessories including the temperature thermistors, the DO sensor, any built in barometer to the hand held display, and the pocket altimeter-barometer (if used). These may include but are not limited to:

1. checking the temperature-display thermistors in the DO sensor against a certified thermometer over the normal operating range of the instrument
2. reconditioning the DO sensor if it fails a performance check
3. confirm batteries are fully charged and electrical connections are clean
4. test instrument to ensure it will read less than 0.2 mg/L in a DO-free solution
5. calibrate the pocket altimeter-barometer (or barometer built into the display) per manufacturers instructions for measurements uncorrected to sea level

### 5.2.2.5 Other Probe-based Sensors or Ion-Specific Electrodes (ISE) Used in Multi-parameter Instruments

The smaller diameter (~1.75") multiparameter probes/minisondes offer generally at least four (4) sensor ports in addition to temperature (standard in all sondes) and depth. The larger diameter sondes (3.0 to 3.5 inches O.D.) may offer ports for 9 or more sensors depending on the manufacturer and model. WRD chose not to include turbidity as a required parameter in the core set. This allows Networks greater flexibility to select from one of several sensor options to fill the 5<sup>th</sup> parameter port on some of the smaller diameter multiprobes and several sensor options to fill remaining ports in the larger diameter multiprobes/datasondes. Thus, Networks should determination based on their data objectives, what additional sensor-based field measurements (if any beyond those required) are most useful to collect Network-wide or at a given monitoring station when using multi-parameter instrument(s). In general, these additional ion selective electrodes/sensors often require a higher level of maintenance at more regular intervals (e.g. Chlorophyll  $\alpha$ ) during deployment and are best applied only to meet highly specific needs of focused studies. Replacement costs for many of these additional sensors when deployed long-term can also be significant.

At this time, ion-specific electrodes (ISE) or sensors that are available for Networks to select from include nitrate-nitrogen, ammonium-nitrogen, ammonia-nitrogen, chloride, total dissolved gas, and, chlorophyll a. In addition, depth (vented and non-vented levels) and ORP may have ports specific to that sensor or may be combined with another sensor (e.g. ORP with pH). With the exception of the depth/level measurement that must be made in the field and ORP measurements (made most accurately in the field), these ion specific measurements are routinely analytically determined in the lab and typically with greater accuracy than those performed in the field using a probe. However, the high frequency of measurement associated with continuous monitoring is generally not practical when lab analysis methods are employed, so situations where a higher frequency of sampling is desirable or facilitated by the use of field probes, some sacrifice of accuracy relative to that obtained by a lab analysis may be deemed acceptable.

Several of these additional or optional sensors measure a potential relative to a reference electrode (often the reference electrode for the pH probe). The Nernst equation describes a linear relationship between the logarithm of the selected ion activity and the observed voltage. In general, ion selective electrodes have a tendency to (1) stabilize less rapidly (particularly after exposure to pH buffers) and (2) drift more than the pH electrode so require shorter maintenance intervals. This requires that they be calibrated on a more regular basis than the core parameters.

What follows is a brief discussion of these other ion-specific sensors plus that for turbidity. These discussions are generally more abbreviated than sensor discussions for the required parameters and the reader is therefore directed to other sources

(manufacturers, USGS HIF) for more detailed discussions. Turbidity is discussed in greater depth because of the anticipated widespread utility of the turbidity sensor, recent significant advances in its development and in situ deployment, and its potential use by multiple Networks.

#### **5.2.2.5.1 Turbidity**

Turbidity is an optical property of a fluid that describes the amount of light that is scattered by suspended solids. A higher intensity of scattered light directly correlates to higher turbidity. Suspended silt and clay are typically the primary causes of turbidity but other contributors to turbidity include finely divided organic and inorganic matter, some soluble colored organic compounds, plankton and microscopic organisms (APHA, 1992). Bed load material (sand and coarser material moving by saltation) may contribute to measured turbidity if the sonde is deployed on or near the bottom of a turbulent stream during periods of high flow. Water clarity or presence of cloudiness (turbidity) is used routinely as an indicator of the condition and productivity of an aqueous system (NFM, 1998). The correlation of turbidity with total suspended solids (TSS) is strong but only approximate because the highly variable refractive properties of the substances that generate turbidity, are not directly proportional to their dry weight used to quantify suspended sediment.

Turbidity, measured in nephelometric turbidity units (NTU), is relatively quick and easy to obtain and can predict about 80% of the variation in suspended sediment concentrations (MacDonald et. al., 1991). Turbidity therefore serves as a reasonable qualitative surrogate for suspended sediment measurement. Turbidity also serves as one of the more sensitive measures of the affect of various land use activities and is an important parameter when interpreting water quality data overall due to its strong correlation to discharge or flow. Several other measurements can be qualitatively correlated with turbidity, provide some indirect measure of water cloudiness, or their measurement is affected by suspended material in the water column. These other measurements include Secchi depth, transmissivity, and photosynthetically active radiation or PAR. Turbidity measurements are a common means of monitoring watershed impacts resulting from fires due to the associated increase in suspended sediment load of streams.

##### **5.2.2.5.1.1 Measurement Theory**

Turbidity sensors operate differently than the sensors discussed in preceding sections that convert electrical potentials to the measurement of the parameter of interest. A turbidity sensor operates by directing a beam of light from a light-emitting diode into the water and measuring the light that scatters off the suspended particles present (Wagner et. al., 2000). There are three basic techniques used to measure turbidity. They include transmissometer, backscatter, and nephelometric. The techniques differ on the angle of reflection of the scattered light from the source to the receiver (i.e. 0°, 120° to 160°, and 90° respectively).

The **nephelometric turbidity probe** (nephelometer) is used most commonly in field applications, often in conjunction with other sensors in a multiparameter arrangement which is a convenient means of monitoring turbidity along with other field parameters. Components of a typical nephelometric turbidity probe include a LED light source with a wavelength of 860 nanometers (near-infrared emitter), a photodiode detector, a pair of optical fiber cables connected to emitter, and detector that intersect the probe face at opposing 45 degree angles so the net angle between the cables is 90 degrees. Light from the emitter enters the sample via one set of fiber cables and scatters off the particles. The light scattered at 90 degrees enters the detector via the other set of optical fiber cables and is measured by the photodiode detector. Most submersible instruments now come with a probe wiper (YSI) or shutter system (Hydrolab) to keep the optical windows clear of fouling substances that tend to build up and distort turbidity measurements during longer deployments (e.g. in continuous deployments). A turbidity probe wiper consists of a wiper motor, wiper sponge and wiper blade (YSI Technical Guide).

**Compact, ex situ turbidity instruments such as the HACH 2100P are also available for use in the field.** This instrument provides near laboratory grade measurements for use in checking or comparing measurements made in situ with a multiparameter instrument. It may also be an option when sondes are not configured with a turbidity meter.

In multiparameter instruments (sonde), a circuit board quantifies sample signal relative to previously measured turbidity standards and generates a value in NTU. This hardware also controls the mechanical wiper causing it automatically to rotate at some prescribed interval in the unattended mode. The wiper may also be triggered manually from the keyboard when operating in the discrete mode (e.g. synoptic sampling) or during calibration.

The more typical measurement range for field turbidity probes is 0 to 1000 NTU but some newer instruments will measure up to 1500 NTUs. As particle concentration increases light scattering intensifies to a point where multiple scattering occurs and light absorption becomes significant. At this point the response is non-linear and the upper limit of turbidity measurements is reached. Instruments that shorten the path length of the light tend to increase the upper range in which turbidities may be measured. A two to three percent difference from NTU standards is typical for measurements made in the 40 to 950 NTU range. The percent difference relative to standards at the lower range of turbidity measurements (<20 NTU) can often exceed 10 percent (USGS Hydrologic Instrumentation Facility, HIF). Significant improvements are being made in field turbidity instruments and it is recommended that instrument performance be investigated before equipment selection. Consultation with the USGS Hydrologic Instrumentation Facility (HIF) who tests the performance of various field equipment used in water quality monitoring is one such source of information.

#### 5.2.2.5.1.2 Calibration and Units

Due to the variety of turbidity instruments available, only a general discussion of instrument calibration is warranted in this guidance. Network technicians are directed to the calibration and operations manuals provided by the specific equipment manufacturers for appropriate calibration procedures to follow. In general, turbidity calibrations involve several common steps. The general steps are laid out and discussed in Section 6.7.2 of the NFM with calibration guidance for submersible turbidity sensors (recommended) provided in Section 7.7.2.B. (Appendix C-1); Wagner and others, (2000) (Appendix C-3); and Wilde and Gibbs (1998). The latter reference and the NFM is also a good source of directions for preparation of stock (usually formazin based) turbidity standards, however these may have a shorter shelf life than standards acquired commercially. It is anticipated that most networks will eventually, if not initially acquire multiparameter instruments that include a turbidity sensor due to its widespread utility and relative ease of use for in-situ measurements.

The response of the turbidity sensor to a calibration standard is a function of the excitation wavelength used in the source emitter. Because the wavelength used in these sensors can vary somewhat among instrument vendors, they **should each be consulted for the acceptable standards to use in the turbidity calibration of their instrument.**

Major components/steps to follow in the calibration of immersion turbidity probes (Procedure A of NFM covering entire bundle of sensors with turbidity) include the following:

1. Preparation or purchase of several turbidity calibration standards (e.g. formazin) and turbidity free water that bracket the expected range of turbidity values for purposes of instrument calibration or checking factory calibrated instruments.
2. Consult the instrument calibration manual to determine if the turbidity sonde is temperature compensated.
3. Prepare a turbidity calibration graph/curve by plotting the instrument reading versus turbidity standard value from a series of repeat measurements on various standards. Allow sufficient time for each measurement to stabilize and rinse sondes thoroughly with deionized water followed by turbidity free water between each measurement.

Currently, **the NTU or nephelometric turbidity unit of measurement for turbidity** is nearly universally applied in both regulatory and non-regulatory arenas. It is the recommended unit to be used for all calibration, measurement, and reporting of turbidity under this guidance. Formazin turbidity units (FTU) are considered comparable in value to NTU and are the unit of measurement when using spectrophotometric equipment. Prior to 1970, other measures of turbidity such as the Jackson turbidity unit (JTU) was found to be problematic due to its usable range, effect of dark colored



particles, and limited measurement of fine particles. The **secchi disk, used to measure water clarity**, also has relatively limited application, is operator sensitive, and more qualitative. As a result, turbidity measurements are gaining favor and the NTU is generally accepted as the standard unit for measuring turbidity. as it is believed to offer the best opportunity for achieving data comparability on a Servicewide basis and performing trend analysis over the long term.

#### 5.2.2.5.1.3 Measurement and Accuracy

There are three general measurement methods for turbidity. They include the nephelometric/turbidimetric method using a curvette-based turbidimeter; **determination by submersible sensor using a multiparameter sonde that includes a turbidity probe**; and the adsorptometric determination using a spectrophotometer. This guidance focuses on the submersible sensor method because **turbidity measurements are best carried out on site and preferably in-situ to avoid biased results from biodegradation, settling, or sorption of particulates in the sample, and various precipitates caused by changes in sample pH during handling/transport**. Other sources of bias include, colored sample solution, gas bubbles, condensation and scratched or dirty cells (NFM, 1998). However, compact turbidimeters are now available that can be readily transported to the field and offer another option from the multiparameter instrument.

In-situ measurement of turbidity using multiparameter submersible sensors has generally not attained the level of accuracy required in a regulatory environment (e.g. USEPA Method 180.1.) This is particularly true for the higher resolution/sensitivity required in the low end of the NTU range in meeting water supply source requirements (0.5 NTU legal limit for drinking water). Thus, the intended use of the data is important in the selection of appropriate measurement methods and equipment. However, for extensive long term monitoring conducted under the NRC/Vital Signs initiatives, where a broad range of conditions occur and cost and ease of measurement are important considerations, the submersible turbidity sensors used in multiparameter probes at continuous/intermittent monitoring stations appear to be the most reasonable alternative. Wagner and others (2000) discuss the use of the turbidity sensor in multiparameter sondes and provide instrument acceptance criteria along with this sensor's calibration, operation, and maintenance (Appendix C. 5-1). Network technicians are referred to this discussion and that found in the NFM for further overall guidance on field turbidity measurements. Information provided by the manufacturer's operations manual however should be the ultimate source for specific direction in the field application of these sensors.

The measurement range of the submersible turbidity sensor should be at least from 0 to 1000 NTU and accuracy the greater of  $\pm 5$  percent or 2 NTU should be achievable (Table C. 5-1). Some sensors may measure turbidity up to 1,500 NTU reliably and these should be considered when high turbidities are anticipated. Generally, sensors that are maintained and calibrated routinely can be expected to provide relatively

error free data. When troubleshooting, consult the guide provided by Table 6.7-3 of the NFM, the manufacturer's operations manual and for submersible multiparameter devices, the discussions of Wagner and others, (2000) in Appendix C-3.

#### 5.2.2.5.1.4 Reporting

This guidance recommends **reporting turbidity data in nephelometric turbidity units or NTUs**. The NTU is the most widely accepted standard unit in field application and there appears little justification or basis to depart from this norm in the perspective of WRD. It should also be noted in the metadata the type of turbidity instrument used and if the instrument is temperature compensated. Wherever possible, use of temperature compensated turbidity instruments is recommended. Table 6.7-4 of the NFM provides guidelines for reporting turbidity measurements that are generally applicable to Networks, although instrument manufacturers are currently supplying equipment of greater accuracy and precision than suggested by these guidelines. Small negative turbidity values (-0.1 to -2.0) may be observed in very clear natural waters and these simply reflect accuracy of the measurement when turbidity is essentially absent. Measurements below negative 2.0 NTU indicate the instrument should be recalibrated with a zero NTU standard. Negative NTU values near zero should be reported as 0 NTU. Independent checks of the multiparameter turbidity sensor with a laboratory grade portable instrument such as the Hach 2100P are recommended.

#### 5.2.2.5.1.5 Maintenance, Cleaning & Storage

Turbidity meters are best maintained by regular testing and inspection of the equipment. At a minimum, test equipment before each field mobilization and ensure it is cleaned prior to or upon return from the field. Manufacturer's instructions and an up-to-date logbook should accompany the instrument at all times. The instrument should be protected from extreme temperatures and the instrument LED display panel should be shielded from direct sunlight. For submersible turbidity probes it is important to ensure that optical surfaces are not damaged during cleaning, operation, or storage and that moist lens cleaning paper or lens-cleaning cloth is used on all surfaces. Scratched or damaged sensors require replacement due to the likelihood that measurements would be affected. The wipers or shutters should be tested regularly and activated prior to each calibration measurement.

#### 5.2.2.5.2 Nitrogen (various forms)

Nitrogen in surface water is considered a nutrient that may occur in dissolved or particulate form and result from **inorganic** or **organic** sources. The dissolved, inorganic form of nitrogen is most available for biological uptake and chemical transformation that can lead to eutrophication of water bodies. Inorganic forms of nitrogen are **ammonia** ( $\text{NH}_3$ ), its more common oxidized form, **ammonium ion** ( $\text{NH}_4^+$ ), **nitrate** ( $\text{NO}_3^-$ ), and **nitrite** ( $\text{NO}_2^-$ ). Nitrite is rare in unpolluted waters. Under high pH conditions, nitrogen in the form of un-ionized ammonia ( $\text{NH}_3$ ) may be present and can be toxic to aquatic life.

The organic form of nitrogen is typically un-ionized ammonia ( $\text{NH}_3$ ) that primarily results from the bacterial decay of humic matter or urea from animal or human waste (agricultural waste lagoons or POTWs). These organically sourced forms of nitrogen occur in various molecular chains of H-N or C-H-N with limited biological uptake (10-20%) potential. However, ammonia ( $\text{NH}_3$ ) is a more toxic form of nitrogen with an aquatic life toxicity that varies with pH and temperature. The NPS Contaminants Encyclopedia will soon be supplemented with a comprehensive discussion of ammonia/ammonium (<http://www.nature.nps.gov/toxic>) and the reader is directed to the in-depth discussions of ammonia in this document.

Kjeldhal nitrogen is determined through lab analysis. It is sometimes reported from lab analyses that determine nitrogen in the trinegative state when ammonia nitrogen is not removed in the initial procedure. It is the sum of the nitrogen contained in free ammonia and other nitrogen compounds which are converted to ammonium sulfate under specific digestion conditions. This method does not account for nitrogen in the form of azide, azine, azo, hydrazone, nitrate, nitrite, nitril, nitroso, oxime, and semicarbazone (APHA, 1998)

Mineralization of soil nitrogen occurring as organic matter usually converts it to ammonia ( $\text{NH}_3$ ), but ammonia is generally not as mobile as ammonium and has a tendency to be oxidized to the ammonium ion before migration is significant unless the pH conditions are quite basic (MacDonald et. al., 1991).

#### **5.2.2.5.2.1 Nitrate-Nitrogen**

The nitrate-nitrogen field measurement employs an ion-selective electrode or sensor to measure nitrogen in the dissolved form as nitrate ( $\text{NO}_3^-$ ). Nitrate is a bioavailable form of nitrogen which aquatic plants can absorb and incorporate into proteins, amino acids, nucleic acids, and other essential molecules. Nitrate is highly mobile in surface and groundwater and may seep into streams, lakes, and estuaries from groundwater enriched by animal or human wastes and commercial fertilizers. High concentrations of nitrate can enhance the growth of algae and aquatic plants in a manner similar to enrichment in phosphorous and thus cause eutrophication of a water body. Nitrate also presents a human health concern particularly to infants that can develop blue-baby syndrome at relatively low levels of nitrate in water supplies. In most natural waters, inorganic nitrogen as ammonium or nitrate is not the growth-limiting nutrient unless phosphorous is unusually high (see section below for sensor discussion).

#### **5.2.2.5.2.2 Ammonium and Ammonia-Nitrogen**

Ammonium ( $\text{NH}_4^+$ ) and ammonia nitrogen (its uncharged form) are also bioavailable to plants including phytoplankton. When ammonium ion is in high concentrations in natural waters containing oxygen, it is oxidized to nitrate by bacteria in the nitrification process. This microbial facilitated redox reaction consumes oxygen at a ratio of 4.5 mg of  $\text{O}_2$  to every 1 mg of  $\text{NH}_4^+$ , thus rapidly depleting available oxygen for

aquatic organism respiration. At higher pH (above 7.5 or 8.0), the  $\text{NH}_4^+ \rightleftharpoons \text{NH}_3$  equilibrium reaction begins to favor ammonia, which is directly toxic to aquatic life because it may be taken up through membranes, and interferes with cell metabolism. Greater than a pH of about 9.2, ammonia becomes the dominant species. Higher temperatures also favor the uptake of ammonia (movement across membranes, e.g. gills) of aquatic organisms such that the Chronic Criteria (CCC) for aquatic organisms such as fish are lowered as temperature increases. Wastewater treatment plants (WTP) and confined animal feeding operations (CAFO) are also potentially significant sources of ammonium.

The ammonium/nitrate sensor works exactly like pH employing a silver/silver-chloride wire electrode in a custom filling solution except the sensor is a polyvinyl chloride (PVC) membrane that is selective for the analyte rather than a glass bulb selective for  $\text{H}^+$  ions. A nonactin membrane separates the internal solution from the sample medium and this membrane selectively interacts with ammonium ions. The sensor module contains a static concentration of the analyte that binds to the inner membrane. The potential that is generated is related to the analyte concentration using the Nernst Equation (YSI, 6-Series Technical Guide). The sensor is unsuitable for use in brackish or salt water due to the abundance of interfering ions (sodium and potassium) that produce large errors.

When used concurrently with determined values of pH, temperature, and conductivity, the same sonde software packages can also provide the user with the concentration of free ammonia ( $\text{NH}_3$ ). The ammonium membrane module is generally **limited to use at depths less than 50 feet to avoid permanent damage to the sensor**. Generally, three calibration solutions/points with the third solution being at a temperature at least 10 degrees Celsius different from the ambient temperature is recommended.

#### 5.2.2.5.3 Chloride

Chloride ( $\text{Cl}^-$ ) is the only common oxidation state for the element chlorine. Because specific conductance is a required parameter and chloride ion can be a significant contributing ionic constituent to the specific conductance measurement, chloride is often not an essential parameter to measure separately (with a probe) unless there is some site-specific reason to monitor it in situ. Chloride is more typically determined and accurately measured through lab analysis of major anions.

Chloride is a chemical component of common rock-forming minerals and consequently is present in various concentrations in surface water primarily depending upon chloride content of meteoric waters, an area's rock type, and anthropogenic inputs. Sedimentary rocks, particularly evaporites, are a principal source of naturally occurring chloride ion in some surface waters. Rainwater close to the ocean may contain from 1 mg/L to several tens of milligrams per liter of chloride with only a few tenths of mg/L for an average chloride content of rainfall across the U.S. (Hem, 1970). Volcanic eruptions and associated air deposition may also be important natural sources of chloride to the

environment. Major anthropogenic sources of chloride in surface waters include POTWs, road salts, industrial discharges, and chemicals used to control dust.

Chloride is highly mobile (conservative contaminant) in the environment but is of low toxicity. EPA (1999) Freshwater Acute Criteria (CMC) and Freshwater Chronic Criteria (CCC) are 860 mg/L and 230 mg/L respectively. However, some States have set standards for chlorides for waters having aquatic life propagation in the 50 mg/L (Minnesota) to 500 mg/L (Illinois) range. Typical concentrations of chloride reported by the USGS for 289 large rivers in the U.S. was 6.7 mg/L, 14.9 mg/L, and 53.3 mg/L for the 25<sup>th</sup>, 50<sup>th</sup>, and 75<sup>th</sup> percentiles, respectively (Hem, 1970).

In performing field measurements of chloride, a sensor comprised of a solid state membrane attached to a conductive wire is immersed in water and generates a potential that depends on the amount of chloride in the medium. The potential is read relative to the reference electrode of the sonde pH probe. The Nernst equation describes the linear relationship between the logarithm of the chloride activity (or concentration in dilute solutions) and the observed voltage (YSI Tech 6-Series Tech. Guide). Because the Nernst equation predicts the chloride sensor response only under ideal conditions, empirical calibration of the electrode is necessary to establish the slope of the response curve. Chloride is a major anion and most accurately measured in the lab along with the analysis of other major ions. However, when monitoring significant short-term changes in chloride concentrations is an important objective of a study, continuous or the more regular monitoring of chloride that is possible with a field probe may be warranted.

#### **5.2.2.5.4 Oxidation-Reduction Potential (ORP/Eh)**

The oxidation-reduction potential (ORP/REDOX) of water is typically measured to determine the overall oxidizing or reducing ability (potential) of the water body. While pH values characterize the relative state of a water to receive or donate hydrogen ions (act as an acid or base), ORP values characterize the relative state of a water for gaining or losing electrons. Field probe-measured REDOX is often difficult to interpret because the controlling REDOX reaction is rarely known or understood. Without knowing which REDOX reaction controls the potential, the measurement is “nonspecific” and of limited use. ORP values are affected by all oxidizing and reducing agents and reflects the combined effects of all the dissolved species in the medium. ORP data is prone to “over interpretation” unless specific chemical information (dominant redox active species) about the water body is known. Much of the use in past surface water monitoring applications has been limited to that of the wastewater treatment industry where the ORP sensor is utilized to document the presence of excess chlorine (oxidizer) in effluent (presence of chlorine generates a large positive ORP value). ORP/Eh measured by a sensor immersed in a solution should not be equated with thermodynamic Eh.

The ORP sensor is also deployed in groundwater monitoring applications where characterizing the redox condition of groundwater aquifers is important in assessing

natural attenuation of organic contaminants such as fuels and chlorinated solvent compounds. ORP measurements are most useful when the user knows one component (oxidizing or reducing compound) in the sample/natural water is primarily responsible for the observed value. This is often problematic in surface waters, however, ORP values tend to generally correlate well (directly) with dissolved oxygen (i.e. oxic conditions correlate with more positive ORP values and anoxic conditions have lower or more negative ORP values). ORP can be useful in characterizing seasonal stratification that can occur in non-flowing water bodies. Suboxic conditions that foster reducing conditions may develop in stratified water bodies such as at/near the bottoms of lakes with poor circulation.

The ORP sensor is a glass imbedded platinum ring with the solution potential read versus the pH reference electrode. The sensor has an operating range of minus 1000 to plus 1000 millivolts (MV) with the range of natural waters extending from +800 to -800 millivolts. The ORP of the sample is determined by measuring the potential of the chemically inert (platinum) electrode, which is immersed in the solution. The ORP calibration typically employs a single standard such as a Zobell solution (e.g. Platinum electrode with Ag/AgCl reference electrode of 4.00M KCl) provides a +228 MV at 25° C reading or another prepared standard such as Light's solution (see Standard Methods, 1998, 20<sup>th</sup> ed.). These are used only as an adjustment of offset, which the instrument is zeroed against. Because the ORP value is temperature sensitive but not temperature compensated, the calibration requires that the user record the temperature of the standard before entering the value of the standard's millivolts. Calibration of the ORP sensor is relatively quick and straightforward but instrument-specific manufacturer's instructions should always be followed in any sensor calibration.

Calibration by manufacturers of the ORP sensors referenced to differing half-cell redox reactions (e.g. Ag/AgCl half-cell reaction used by YSI and In-Situ vs. Hydrogen half-cell reaction used by Hydrolab) can result in ~200 millivolt difference when the ORP measurement is based on a vendors calibration (not re-calibrated to the same millivolt standard). In-Situ provides an equation to normalize the readings reported by their sensor calibrated with their standard solution to the standard hydrogen electrode values ( $\pm 50$  mV). Common calibrations standards for ORP include Zobel solution, Light's solution and standards made from dissolving quinhydrone reagent in de-ionized water.

#### **5.2.2.5.5 Chlorophyll $\alpha$ (from total fluorescence)**

Chlorophyll is a key biochemical component in the molecular apparatus that is responsible for photosynthesis and is found in various forms within the living cells of algae, phytoplankton, and other plant matter of water environments. Like other biological response variables, chlorophyll  $\alpha$  tends to integrate the stresses of various parameters over time, and thus is often an important nutrient-stress parameter to measure (see Part B for additional details).

The amount of chlorophyll in a water sample is a general measure of the concentration of suspended phytoplankton that also can be used as an indicator of water quality (see Section 10200 A of Standard Methods for the Examination of Water and Wastewater). Three methods for the determination of chlorophyll  $\alpha$  in phytoplankton include spectrophotometric (ALPHA 10200 H.2), fluorometric (ALPHA 10200 H.3), and high performance liquid chromatography or HPLC (ALPHA 10200 H.4). The spectrophotometric and HPLC methods are a more classical approach performed in a laboratory and involve (1) filtration of a water sample to concentrate the chlorophyll containing organisms, (2) mechanical rupturing of the collected cells and (3) extraction of the disrupted cells into the organic solvent acetone before analysis by one of these two methods. These methods have been shown to provide accurate and reproducible results for scientific reporting.

A key characteristic of chlorophyll that permits **approximate** in-situ measurements of chlorophyll  $\alpha$ , is its **ability to fluoresce when irradiated by a light source** (light emitting diode or LED) **of approximately 470 nm**. The sensor operates under whole-cell, heterogeneous conditions, so when irradiated by light of this wavelength the sensor will measure, at least to some degree, everything that fluoresces in the 630 to 730 nm region of the spectrum (YSI Series 6 Technical Guide). Thus, the sensor actually measures **total fluorescence** and the amount of chlorophyll  $\alpha$  present is some fraction of this total. Although there is a potential loss of accuracy with the fluorometric method, this method does permit the facile collection of large amounts of chlorophyll data in either spot sampling or continuous monitoring applications.

There are **several sources of error** inherent in in-situ application of the fluorometric method that should be considered (along with DQOs) before choosing to deploy the chlorophyll  $\alpha$  sensor. These include interferences from turbidity and other fluorescent species, the limited optical flexibility of sonde-type fluorometers with fixed optical configurations, sensor fouling/scratching/bubbles on the optics and effectiveness of mechanical (wiper) cleaning of the optical face, temperature effects during calibration and measurement, the general lack of good calibration reagents, and the variation/quality of calibration standards and methods.

For these reasons, WRD recommends Networks only deploy (at least initially) chlorophyll  $\alpha$  sensors under spot sampling conditions where a very focused need and purpose has been identified and where a certified extractive analysis procedure may be performed on a few samples combined with probe monitoring to determine or bound measurement error. Network staff should consult various manufacturer and other publications in determining the appropriate application of this sensor prior to its deployment as its utility may be limited or problematic in many situations.

#### 5.2.2.5.6 Total Dissolved Gas

Nitrogen ( $N_2$ ), oxygen ( $O_2$ ), and carbon dioxide ( $CO_2$ ) are significant components of the earth's atmosphere and consequently are found as dissolved gases in surface waters as a result of their atmospheric partial pressures. Methane ( $CH_4$ ), hydrogen sulfide

(H<sub>2</sub>S), and nitrous oxide (N<sub>2</sub>O) are common dissolved gases in water environments that are anoxic and typically occur as products of biogeochemical processes (Dissmeyer, 2000). Nitrogen and oxygen are the two atmospheric gases that when present under conditions of supersaturation, can lead to gas bubble disease in aquatic organisms. A sensor is available that measures **total dissolved gas pressure (TGP)** directly using the membrane diffusion method. The sensor utilizes a gas permeable membrane tube that is permeable to all gases including water vapor (membrane most closely models the behavior of fish gills). The probe is subject to biofouling, but only the response time and not the calibration is affected.

Surface water can become supersaturated with respect to dissolved gases by various means including heating, air entrainment in spilled or pumped water, intensive photosynthesis, and through turbulent flow (rapids) or waterfalls (e.g. those associated with dams and spillways). The primary sign of gas supersaturation is the formation of bubbles on submerged surfaces or within the vascular systems of tissues of aquatic organisms. **Gas bubble disease** is a condition that affects a wide variety of fish and other aquatic animals in both fresh and saline water. Symptoms include gas bubbles or blisters in the fins of fish and behind the eyeballs to produce “pop-eye”. The Columbia River System has experienced serious mortalities in aquatic species due to gas bubble disease (USGS WRIR 01-4005).

Despite recognition of symptoms of gas bubble disease in fish and other aquatic life since the turn of the 20<sup>th</sup> century, only limited monitoring of total dissolved gas has occurred. Its application to water quality monitoring has largely been by the wastewater treatment industry. Because a specific sensor is available for oxygen and that parameter has significant importance in assessing water quality (e.g. aquatic life standards), as well as indicating if supersaturated conditions exist, total dissolved gas measurements are generally not made in conventional surface water quality monitoring.

#### 5.2.2.5.7 Depth and Vented Level

Sondes can be equipped to measure either depth or level. Both depth and level measurements use a differential strain gauge transducer to measure pressure with one side of the transducer exposed to the water. By convention, **depth refers to unvented measurements where the other side of the transducer is exposed to a vacuum** while **level measurements are vented to the surface, thus having one side of the transducer exposed to the atmosphere**. The depth transducer measures the pressure of the water column plus that of the atmosphere. Depth must be calculated from the pressure exerted by that of the water column alone, so when depth is calibrated in air prior to probe deployment, the software records the atmospheric (barometric) pressure and subtracts that pressure from all subsequent measurements. Because **atmospheric pressure will change from that to which the instrument was calibrated at the time of deployment, a small error in the depth measurement equal to 0.045 feet for every 1 mm Hg change in atmospheric pressure will occur over the sondes deployment**. Generally, highly accurate depth measurements are not necessary unless the data is used in the determination of **flow/discharge**. In those situations, a **level sensor should be used** in



place of a depth sensor to account for changes in atmospheric pressure during probe deployment (YSI Series 6 Technical Guide).

In performing level measurements the transducer is vented to the atmosphere, which removes the effects of changing atmospheric pressure from that of the time of calibration. Thus the transducer measures only the pressure exerted by the water column and the vented level (shallow) can be used more accurately in the calculation of flow. Level transducers (secondary device) may be used in conjunction with a weir or flume structure (primary device) to calculate flow. The shallow vented level coupled with the Manning equation may also be used to calculate open channel flow under favorable conditions. The channel itself is the primary measurement device and the flow can be calculated from the level of water in the channel. This method can be accurate to 10% (see also section 5.2.4.3).

The reader is directed to the specific instrument manufacture's probe operations manuals for procedures to follow in setting up and enabling sensors to measure stage or water level (vented) in the determination of flow under a variety of conditions. USGS hydrologic sources such as WSP 2175 (Rantz et. al., 1982) on techniques of measuring flow should be consulted as well.

#### **5.2.2.6 Photosynthetically Active Radiation (PAR)**

For marine/estuarine environments, light attenuation or photosynthetic photon flux density (PPFD) is often measured as photosynthetically active radiation or PAR to better understand the potential productivity of the water body. LI-COR Biosciences is a leader in the development of underwater quantum sensors and offers two instruments that measure PAR in aquatic environments. They are the LI-192SA Underwater Quantum Sensor and the LI-193SA Spherical Quantum Sensor. Both sensors utilize computer-tailored filter glass to achieve the desired quantum response (i.e. PAR, 400 to 700 nm range). Calibration of the instrument is NIST traceable. For best results it may be necessary for two PAR sensors, one submerged and one in air (LI-190SA), to be deployed and connected to a single data logger (LI-1400) to remove effects of changing radiation conditions due to waves, swells or atmospheric conditions (clouds). Similar set ups may also be used in vertical profiling and in conjunction with multi-parameter instruments. The marine workgroup has strongly recommended the collection of PAR data where feasible because of its utility and collection under the EMAP Program (see Marine Workgroup white paper at <http://science.nature.nps.gov/im/monitor/deskref.htm>). However, it is an expensive parameter to obtain. Marine Networks are referred to the LI-COR Biosciences website at <http://www.licor.com> for instrument specifications and accessories.

#### **5.2.2.7 Quantitative/Qualitative Flow/Discharge (Flowing Water Bodies) and Stage/Level Measurements (non-Flowing Water Bodies)**

Servicewide, the **quantitative measurement or qualitative estimate of**

**flow/discharge is being required** (i.e. is a core parameter) at all flowing water bodies under freshwater conditions. Similarly, a **stage or level quantitative measurement or estimate is required** for all non-flowing fresh water bodies. Methods for measuring and estimating flow/discharge and stage/level are discussed in following sections.

#### 5.2.2.7.1 Quantitative Flow Measurements of Flowing Water Bodies (Streams)

The science and art of measurement and computation of streamflow has long been a subject of much investigation, discourse, and innovation among its practitioners. In the release of Water-Supply Paper 888, D. M. Corbett and others (1943) of the USGS published one of the first manuals on stream-gaging procedures and equipment. Subsequent later developments in techniques and equipment by the USGS have resulted in supplementary reports that update this classic paper. A detailed, two-volume set on this subject entitled “Measurement and Computation of Streamflow” covering measurement of stage and discharge (Vol. 1) and computation of discharge (Vol. 2) was released by the USGS as Water Supply Paper 2175 in 1982 (Rantz et al, 1982).

Over the years, selected aspects of discharge/flow measurements have been presented in various USGS publications ranging from open-file reports to the published series titled “Techniques of Water Resources Investigations”. Other federal agencies (USDA) and international organizations have produced similar but less detailed guidance. For a condensed but practical guide to field techniques in installing a staff gauge and measuring discharge, Network staff are directed to Chapters 9 and 10 USDA General Technical Report RM-245 by Harrelson and others (1994). Network staff is directed to Book 3 of the NFM “Applications of Hydraulics” for more recent, detailed discussions of stream flow measurements covering a variety of methods at various sites (e.g. under peak and low flow conditions, at culverts, dams, gaging stations, cableways etc).

##### 5.2.2.7.1.1 Theory and Methods

Stream gage locations are selected on the basis of locally available conditions that are most conducive to making stage and discharge measurements accurately and for developing a **stable stage-discharge relation or rating curve**. Ideal conditions include: 1) a straight upstream and down stream section (300 ft. each) from the gage site, 2) total flow confined to a single channel at all stages, 3) a streambed not subject to scour and fill, 4) permanent banks which are high enough to contain floods and that are free of brush, 5) unchanging natural controls (e.g. bedrock outcrop for low flow & channel constriction for high flow), 6) presence of an upstream pool for measurements during extreme low flow, 7) free from effects of confluence with another stream, 8) a reach that is satisfactory for measuring discharge at all stages and 9) a site that is readily accessible.

The stage of a stream or lake is the height of the water surface above an established datum plane. The water surface elevation referred to some arbitrary or predetermined gage datum is called the “gage height” (Rantz et. al., 1982). Gage height

and stage are synonymous and typically measured to an accuracy of 0.01 feet or 0.001 meters. Datums are selected so that reported numbers are always positive to avoid confusion. **Records of gage height are used with a stage-discharge relation (rating curve) in determining stream discharge.** The record of stage may be obtained by systematic observations of a non-recording gage or by means of a water-stage recorder. Recording gages are often enhanced by telemetry systems that transmit gage-height information to locations where it can be closely monitored and used on a regular basis. Rantz and others (1982) discuss several recording and non-recording devices and their accuracy when used in the measurement of stage.

Controls are natural or artificial (man-made structure built to constrict the channel) physical elements that effect or control the stage-discharge relationship. Favorable controls are those which have permanence and foster higher sensitivity of stage measurement such as the above conditions or engineered weirs or flumes. For example, the small notch or V in the central portion of a weir serves the purpose of increasing sensitivity to gage measurements and ultimately the determination of discharge under low flow conditions. Least favorable controls for developing an accurate stage-discharge relationship are those that are unstable or most subject to change by velocity-induced scour and deposition such as natural sand channel streams.

**Discharge (Q) is defined as the volume of water passing a cross-sectional area per unit of time.** It is typically expressed in units of **cubic feet per second or cubic meters per second** and can be calculated simply as velocity times cross-sectional area ( $Q = VA$ ). Several methods exist for measuring discharge but most methods share several similar steps. They include selection and calibration of a **current meter** or other means of determining velocity, proper site selection, dividing the channel cross-section into equal increments (usually 25 or more), making the current measurements (by meter or other means) at several points in the vertical while allowing enough time for the device to stabilize (40 seconds for most current meters), determining the mean velocity at each vertical, tabulating the data in field notes, making field computations using the tabulated data, and field checking the computations with an alternate, usually more approximate measurement method (e.g. float method).

Determination of velocity may be performed by any one of ten (10) or more methods (Vertical-velocity curve, Two-point, Three-point, Surface velocity etc.). Network personnel are directed to USGS WSP 2175 (Rantz et. al., 1982) for detailed discussions of the most commonly employed methods and current meter deployment options, procedures for conventional current-meter measurement of discharge, and a discussion of stream stretch qualities most favorable for obtaining velocity measurements.

The conventional current-meter method is most commonly used in gaging streams. In this method, the type of current meter used (most accurate) is selected based on stream conditions. **Marsh-McBirney, Price AA, and Pygmy current meters** are some of the most common. Area is accurately calculated by measuring depths at several increments along the cross-section or stream transect while a current meter is used to

measure velocity at the same location as each depth measurement (Harrelson et. al., 1994). Initially, **several discharges are computed at various stages at a frequency that enables definition of the station/discharge rating curve for the site.** The stage-discharge relationship may be simple or complex depending on several factors indigenous to the stream and the rate of change of stage. Current meter types, rating tables, deployment methods (cable way, bridge, boat etc.), and discussions of their use in measurement of velocity (at a point) and computation of discharge (from mean velocity), are provided in Rantz et. al. (1982). Special problems posed by the measurement of deep, swift streams (non-wadeable) under adverse conditions and the corrections that must be performed are also discussed.

For recurring discharge measurements at a monitoring location, it is usually best to install a **staff gage** (non-recording) in the absence of any nearby automated (recording) gaging station. A staff gage is a scale (usually enameled steel) placed in a stream to show the elevation of the water surface. It is calibrated by referencing the numbered height on the gage to the surveyed elevation of the water surface and its associated flow at the time of installation. A rating curve or stage-discharge relationship is then developed from numerous stage measurements and discharge computations made at the site during variations in flow by plotting stage versus discharge (typically gage height in feet versus discharge in cubic feet per second) on log-log paper. The more points, the more precise the rating curve is likely to be.

Discharge rating curves are usually determined empirically by means of periodic measurements of discharge and stage using a current meter (minimum of 10 per year is recommended initially). However the rating curve may shift over time and periodic measurements are necessary after the first year to either confirm the permanence of the rating or to follow changes/shifts in the rating. It is important that the rating curve include measurements made at flow extremes (e.g. flood conditions) and under ice conditions to be most accurate. Volume 2 of USGS WSP 2175 (Rantz et. al., 1982) discusses stage-discharge relations ranging from simple to complex and the various parameter variables (slope, velocity index) that should be considered when computing discharge rating curves under more complex situations.

WRD recommends that all long term monitoring stations on flowing water bodies be equipped with at staff gage or other device for measuring flow accurately and that a flow measurement be recorded/determined whenever field measurements or water samples are collected at a monitoring site. Furthermore, Network staff/cooperators performing flow measurements should identify the site conditions anticipated at each monitoring station in the Network and consult the appropriate reference above for appropriate protocols to obtain accurate flow measurements under those site conditions. As in conducting other field measurements, properly measuring flow requires training, experience, and familiarity with the equipment as well as personnel cognizant of safe operating techniques and procedures.

#### 5.2.2.7.1.2 Calibration, Measurement Units & Reporting

Equipment used to measure discharge or flow (e.g. current meters) should be tested/calibrated prior to mobilization to the field. Consult the manufacturers O & M manual for specific calibration methods and appropriate applications for selected current meter and other devices used in the flow/discharge determinations. For Servicewide consistency and where feasible, WRD recommends that **computations of flow be in English units and reported in cubic feet per second**. In general, WRD recommends following various state

(e.g. <http://www.tnrcc.state.tx.us/admin/topdoc/gi/252/swqmproc.pdf>)

or USGS NFM guidance in conducting flow measurements.

#### 5.2.2.7.2 Qualitative Flow/Discharge & Level Estimates

Qualitative flow estimates shall be performed as follows:

**Flowing Water Case** – Qualitative characterization of flow/discharge (e.g., stream/river); **At a minimum, some estimation of flow will be made based on visual estimation of relative % of bank full at the sampling site as follows: (Dry; Low, ≤ 25% of bank full; Intermediate, between 25% and 75% of bank full; High, 75% to 100% of bank full; Flood/Overbank > 100% of bank full).** Alternatively, a similar percent estimation may be made based on the stream hydrograph from **the nearest gaging station on the same reach or in the same reach that is too distant for an accurate quantitative measurement of flow for the monitoring site.** (Note: for some small streams, it may be possible to obtain an approximate quantitative flow measurement simply by using a bucket and a stop watch.)

**Still/Non-flowing Water Case** – Qualitative characterization of water body level or stage (e.g. lake, reservoir, pond, wetland, etc.) in lieu of a water level measurement based on a surveyed-in level/staff gage that may be regularly reported by some water body owner or management agency (BLM, COE, BOR, USGS) that maintains level/stage records.

At a minimum, some estimation of water level for the water body (dry, low, intermediate, high, or in flood (latter implying exceedance of some normal yearly range) should be reported with water quality data. In addition, a **depth profile of basic water column parameters is required** for standing/non-flowing water bodies (lakes, reservoirs, etc.). Where appropriate, WRD will give general guidance on depth profiling to ensure some basic consistency in these measurements. However, both spatial and depth sampling considerations are often site or water body-type specific. Any State guidance should be consulted first in determining appropriate spatial and depth integrated sampling at non-flowing water sites, particularly if monitoring data could be used in some regulatory context.

A **quantitative flow measurement** should be made by gage (staff, wire weight, bubble) or by an instantaneous/manual flow measurement at/near a flowing-water monitoring site in most instances. Quantitative flow is required for Total Maximum Daily Load (TMDL) determinations, in several other regulatory situations, and oftentimes may be required by cooperators where other agencies may choose to use or help fund NPS data collection. Where possible, it is recommended that monitoring be established at an existing gaging station or that a new staff/level gage be established for a monitoring site. A quantitative flow measurement is highly recommended for monitoring stations but is not being required universally or Servicewide by WRD. An example of concise and relatively easy to follow procedures for obtaining an instantaneous/manual flow measurement may be found at <http://www.tnrcc.state.tx.us/admin/topdoc/gi/252/swqmproc.pdf>

### **5.2.3 Manufacturers/Vendors of Multiparameter Probes/Sensors used in Field Measurements\***

#### **5.2.3.1 Introduction**

Below is provided some limited information about a few of the major domestic vendors of water quality monitoring equipment whose products may be applicable for continuous/intermittent monitoring with multiparameter probes. Their listing here is for informational purposes and is **not meant to imply any endorsement of their products or equipment by the federal government or National Park Service.**

#### **5.2.3.2 Yellow Springs Instruments Inc. (YSI)**

YSI was established in 1948 in Yellow Springs OH. The headquarters remains in Yellow Springs and the company has domestic operations in CA, MA, NJ and international sales offices in the UK, China and Japan. The company is owned by the employees and was recognized in 1994 as the ESOP Company of the year. Revenues in 2001 are projected at 59M. The company maintains several certifications including ISO 9001 and ISO 14001. In 2000, US EPA named YSI as a charter member of the National Environmental Achievement Track in recognition of the company's efforts to reduce its ecological footprint.

YSI Environmental's focus is the natural resources market. Their mission is to provide their customers with the tools to obtain the highest data quality. To this end they focus on designing sensors for long-term deployments such as their patented stirring independent Rapid Pulse dissolved oxygen probe and their self-cleaning turbidity and chlorophyll sensors. Recently they have begun marketing of their new Extended Deployment Systems which now include wipers for the DO and pH sensors in addition to the turbidity sensor. All YSI multi-parameter instruments have been designed with advanced diagnostics, which provide users with additional data quality assurance tools. Their Windows based EcoWatch software displays and graphs data easily and quickly. YSI personnel have decades of experience in water quality monitoring including field installations, water chemistry, and sensor technology and data interpretation making their

technical support the one of the best in the industry. Another of the company's strengths is their customer training programs. These are applicable for large groups or individualized to meet a specific customer's requirement.

YSI offers a full range (6 Series) of multi-parameter datasondes, minisondes and single parameter instruments to meet specific needs in continuous monitoring or synoptic sampling as well as handheld displays and software (Ecowatch™).

#### **5.2.3.3 Hydrolab Inc.**

Hydrolab Inc. was started in 1957 and introduced the first multiparameter probe in 1968. They were based in Austin, Texas but have recently (2003) moved their operations to Loveland, Colorado to join the Hach Company. Hydrolab Inc. distributes water quality monitoring products worldwide and has noted several firsts in the water quality monitoring field. The company is one of a few recognized leaders in the water quality instrumentation field and has provided a broad line of water monitoring products and technical support for over 40 years. Their product warranties are among the strongest in the industry. Hydrolab primarily designs and manufactures water quality multiprobes and data displays meant to perform in a variety of water environments from wells (down hole) to marine and fresh surface waters. Hydrolab provides full technical support and can be contacted 24/7 through their 1-800 service number. Their Datasonde 4a measures 15 or more parameters and can be deployed in continuous monitoring, their smaller diameter minisonde 4a will fit down 2" boreholes and the Quanta is a lower cost multiparameter instrument having broad uses in synoptic sampling.

#### **5.2.3.4 In-Situ, Inc.**

In-Situ Inc. is based in Laramie, Wyoming and has been a manufacturer of environmental monitoring equipment for over two decades. Historically, the company's focus has been to provide instrumentation for the ground water monitoring and testing industry including data logging (level) capabilities using their well known Hermit data loggers and Troll level loggers/pressure transducers. Recently, In-Situ has expanded their product line and in-place monitoring capabilities to include water quality with a primary goal to establish themselves as a world leader. They provide a full range of technical support and specialize in the smaller diameter multiprobes for application to the groundwater monitoring industry where small diameter casing is oftentimes a constraint. The MP9000 multi-parameter instrument is the most recent addition to their product line and offers a broad range of parameter measurements in a compact (1.75" diameter) instrument. In-Situ became a GSA approved vendor in July, 2002 (<http://www.gsaadvantage.gov>).

#### **5.2.3.5 Other Equipment Vendors**

There are several other manufacturers of multiparameter water quality monitoring equipment although several of these companies do not offer multi-parameter instruments that include the 4 core water column parameters or an expanded set of probe based

parameter options. Horiba, Stevens Water, Hach (now owner of Hydrolab), BioDevices Corp. and several international firms also provide multi-parameter instrumentation of varying capabilities to the water quality monitoring industry.

#### **5.2.4 Other Important (Non-sensor based) Field Parameters to be Considered at Sites**

At most monitoring stations, WRD recommends that consideration be given to supplementing the four (4) required or “core” water column parameters and a qualitative flow estimate or quantitative flow measurement with two other chemical/biological parameters obtained in the field. WRD “highly recommends” that some form of **biological monitoring** (e.g. macroinvertebrates), and **alkalinity/ANC** be considered and included at all long-term monitoring stations where it is deemed appropriate by Networks on a site by site basis.

##### **5.2.4.1 Introduction**

Some form of biological monitoring, and determination of alkalinity or acid neutralization capacity (ANC) is strongly recommended although not universally required or necessarily applicable to all water body types or all monitoring situations. While these are very important components of monitoring in many situations, their measurement is not being mandated at all monitoring stations. However, in many instances, WRD recognizes their measurement can be crucial to obtaining an adequate data set with which to evaluate the overall health of a water resource or aquatic ecosystem and to establish cause and effect suggested by information from core parameters and vital signs monitoring of other resources (e.g. importance of alkalinity/ANC measurement in characterization of atmospheric acid deposition effects).

Furthermore, in some instances, stresses to biological communities may be the first sign or the only indication of an impact to a water resource, particularly when stressor-related contaminants are unknown or not identified for monitoring early in the monitoring program. Therefore, WRD anticipates that Networks will determine the utility of collecting these important supplemental parameters on a Network wide or monitoring site-specific basis. Any omission of monitoring for these additional parameters at specific monitoring stations or in situations where it would normally be appropriate should be explained/discussed in the detailed monitoring plan to be submitted to WRD.

##### **5.2.4.2 Biological Monitoring**

Biological methods or biocriteria monitoring to assess water quality can take a variety of forms including the collection, counting and identification of aquatic organisms; biomass measurements; measurements of metabolic activity rates; measurements of the toxicity, bioconcentration and bioaccumulation of pollutants; and processing and interpretation of biological data (Standard Methods, 1998, 20<sup>th</sup> ed.).



Common communities of aquatic organisms studied include plankton, periphyton, macrophyton, macroinvertebrates, fish, amphibians, aquatic reptiles, birds and mammals. In such studies, the field observations of the investigator are often critical to meaningful biological interpretations and therefore participation of the biologist in field collections and close attention to field sampling procedures are required.

#### **5.2.4.2.1 Macroinvertebrates**

Macroinvertebrates are bottom dwelling organisms (benthos) that are typically visible by the unaided eye and are retained by the US Standard No. 30 sieve (0.595 mm or 0.600 mm openings). Communities of macroinvertebrates tend to be diverse (roam freely over, live on, in or are attached to various substrates) and relatively abundant in fresh and salt water environments and therefore offer several aquatic assessment options. Standardized bioassessments include species composition, taxa richness, diversity, evenness, trophic levels, and major taxonomic spatial and temporal patterns. Freshwater invertebrates include insects, crustaceans, mollusks, annelids, and flatworms. Major invertebrates in marine/estuarine environments include annelids, bryozoans, sponges, roundworms, insects, coelenterates, crustaceans, and echinoderms (Standard Methods, 1998, 20th ed.).

By monitoring macroinvertebrate abundance and composition (structure), a community's response to changing habitats and water quality may be indicative of impacts by municipal, industrial, or agricultural waste streams and other land uses on surface waters. Macroinvertebrate community change has been documented from four broad changes in environmental conditions including substrate alteration, toxic chemical pollution, and increases in either organic or inorganic micronutrient loading. Assessment of sites believed to exhibit pollution impacts generally requires comparison with unimpacted sites (reference sites) exhibiting a similar habitat. While many biological assessment methods have been established for some time, new method development is ongoing by several organizations including the EPA and many states.

Typically, other site assessment information is necessary to properly interpret biological assessments. These data include dissolved oxygen, substrate type, sediment composition and grain size, water depth, total organic carbon (TOC) and other site- and situation-specific characteristics.

#### **5.2.4.2.2 Pathogen/Fecal Indicator Bacteria**

Use of indicator organisms is the primary means of testing for pathogens in environmental samples. Coliform indicators such as total coliform, fecal coliform, and *E. coli* are most common but fecal streptococci, enterococci, *Clostridium perfringens* and *Aeromonas* have been proposed as water quality indicators as well (EPA has recently approved (June 03) test methods for these latter pathogens; this announcement and links may be found at <http://www.epa.gov/fedrgstr/EPA-WATER/2003/July/Day-21/>. Although the traditional bacterial indicators (total, fecal and *E. coli* coliforms) may not correlate with viruses or parasites in pristine waters or groundwaters and may be of

limited utility in marine/estuarine monitoring, their tests are useful because it is so rare to isolate bacterial enteric pathogens without some fecal contamination (Standard Methods, 1998, 20<sup>th</sup> ed.).

Coliform bacteria consist of several genera belonging to the family Enterobacteriaceae. The definition is method based in that the detection covers a broad group (across genera) that uses lactose fermentation. Thus, all facultative anaerobic, gram-negative, non-spore-forming, rod-shaped bacteria that ferment lactose with gas and acid formation within 48 h at 35 °C are included (APHA, 1998, 20<sup>th</sup> ed.). Fecal coliform tests attempt to distinguish those total coliforms that are related to the gut and feces of mammals and therefore a better indicator of potential to cause illness in humans. *Escherichia coli* (*E. coli*) is a member of the fecal coliform group whose presence in water is diagnostic of fecal contamination. They are defined as coliform bacteria that possess the enzyme  $\beta$ -glucuronidase and are capable of cleaving the fluorogenic substrate 4-methylumbelliferyl- $\beta$ -D-glucuronide (MUG) with the corresponding release of the fluorogen when grown in EC-MUG medium at 44.5 °C within  $24 \pm 2$  h or less (Standard Methods, 1998, 20<sup>th</sup> ed.)

NPS in its role as a land management agency has certain responsibilities for health and safety in the public's use of its facilities. This includes protecting the public from water borne illness and disease and this will often involve monitoring of recreational waters including lakes, rivers, streams, swimming beaches and water supplies used by the public at various park units. In general, monitoring of this type is a requirement of state or local health organizations and should not be funded under the Vital Signs program unless some longer term need and a tie in to long term change or degradation over time in the aquatic resources of a park is suspected.

There are multiple specialized methods and rapid tests for pathogens. However, routine examination for pathogenic microorganisms as part of a long term water quality monitoring program, is not recommended. Pathogen testing is most purposeful in the normal course of compliance monitoring, short term investigations of water-related illness and special investigations. The USGS has begun monitoring trace compounds with endocrine-disrupting potential associated with wastewater discharges. Their **Wastewater method** analyzes for 54 organic compounds (see Part D) that may pass through wastewater treatment plants with little or no degradation or are the metabolites of such compounds that are possibly harmful to aquatic ecosystems. Where Networks conduct monitoring on water bodies impacted from WTPs, lower frequency long term monitoring of these compounds may be another consideration.

#### 5.2.4.2.3 Other Biological Monitoring

Biological monitoring can take as many forms as there are aquatic organisms. Monitoring of aquatic organisms other than macroinvertebrates is also common with fish being a good example as a key indicator component of many natural food webs. They serve as environmental indicators in part due to their position in the food chain and their tendency to respond to changes in flow, turbidity/clarity, temperature regime, pH,

salinity, solutes DO, substrate composition and pollution level. Through fish kills, they are often an immediate and primary indicator of the toxification of streams and lakes. Fish also share many physiological properties with mammals and provide important information over the long term on environmental change that may be occurring and reflected at the population or assemblage levels. Their ecological importance is often complemented by the attention granted fish through commercial and recreational interests. Thus, Networks such as those in Alaska implementing water quality under Vital Signs may find that due to funding limitations, dovetailing the water quality monitoring with ongoing fish monitoring programs provides the greatest access to geographically diverse monitoring sites.

#### 5.2.4.3 Alkalinity and Acid Neutralization Capacity (ANC)

WRD adopts the USGS/NAWQA definition of alkalinity and acid neutralization capacity (ANC) for use in the NPS Vital Signs monitoring program. Thus, **alkalinity will refer to a filtered waters ability to neutralize acid** whereas **acid neutralization capacity (ANC) will refer to the alkalinity of an unfiltered water sample** (i.e. alkalinity due to both dissolved and suspended matter). A waters ability to neutralize acid (i.e. buffering capacity) is largely a function of the **bicarbonate and carbonate ions derived from dissolution of calcium carbonate in the drainage basin**. When there is little input of calcium carbonate to a surface water body, the dissociation of dissolved carbon dioxide is the reaction that may predominate resulting in slightly acidic waters with little buffering capacity.

##### 5.2.4.3.1 Measurement Theory and Methods

Alkalinity is a measure of a waters acid buffering capacity or its ability to neutralize an acid. Alkalinity may be measured in the field or laboratory and essentially all methods involve titrating a water sample with a standard solution of sulfuric acid and monitoring the pH change as the acid is added to the sample. Historically, conventional measurements of alkalinity involved an acid titration with a specified or fixed endpoint such as pH of ~ 8.3 (phenolphthalein or carbonate alkalinity endpoint) and/or pH of ~ 4.5 (methyl-orange or bicarbonate alkalinity endpoint). The acid neutralization capacity or ANC of water was determined primarily for waters of low alkalinity where a more accurate analysis (including alkalinity contributed by suspended sediment) was necessary with the pH endpoints determined analytically (e.g. Gran titration). This “incremental” method is more accurate and recommended/preferred for use by the NAWQA program for both alkalinity and ANC determinations. Rather than assuming the equivalence points to be at pH 8.3 and 4.5, this method determines the actual equivalence points by constructing a titration curve (plotting pH and the volume of sulfuric acid) and selecting the pH at the inflection point of the curve as the endpoint (Shelton, 1994).

The USGS National Field Manual (NAWQA) requires that methods for determination of field alkalinity and acid neutralization capacity use identical electrometric procedures involving the incremental acidmetric titration of a sample with

endpoints determined from the inflection point of the titration curve. By the USGS definition, the only difference in these methods is that the alkalinity samples are filtered (0.45  $\mu\text{m}$ ) and ANC samples are unfiltered, thereby **including in the ANC measurement, any alkalinity contributed by the water body's particulate suspended fraction**. Networks should be cognizant of how definitions of alkalinity and ANC and the methods employed in their determination can differ and affect the reported results. WRD recommends that NAWQA definitions for alkalinity/ANC be used and their protocols be followed to achieve Servicewide consistency in reported measurements.

Alkalinity is typically **caused by anions in natural waters that can enter into a chemical reaction with a strong acid**. These are primarily the carbonate ( $\text{CO}_3^{2-}$ ) and bicarbonate ( $\text{HCO}_3^-$ ) ions. Dissolution of these species is most typically caused by the partial pressure of  **$\text{CO}_2$  in the atmosphere** but their presence may be further elevated in areas of **carbonate rock dissolution** where waters are often of a bicarbonate type (elevated in  $\text{HCO}_3^-$ ). The hydroxide ( $\text{OH}^-$ ) species may also be present when natural waters occur above pH of 8.3 and become a significant contributor to alkalinity. Borates, phosphates, silicates, arsenate, ammonium and organic ligands (e.g. acetate and propionate) can also contribute to alkalinity when present. However, except for unusual natural waters or waters significantly impacted by anthropogenic sources, **non-carbonate ionized contributors are rarely present in large enough quantities to affect alkalinity or ANC determinations** (NFM, 1998).

Field determinations of alkalinity and acid neutralization capacity are recommended because degasification, precipitation, and other chemical and physical reactions can cause the concentrations of bicarbonate and carbonate to change significantly (Shelton, 1994). Alkalinity samples should also be pre-filtered to avoid contributions to alkalinity by particulate matter. The ANC of water is determined from an unfiltered sample and differs from alkalinity in that the solutes **plus** unfiltered particulates are used (titrated with acid) to determine ANC.

NAWQA field methods employ a **digital titrator** to accurately dispense small quantities of acid titrant. The endpoint inflection is then determined by plotting the change in pH per milliliter of acid added. Once the equivalence ( $\text{H}_2\text{CO}_3 - \text{HCO}_3^-$ ) pH is determined, the milliliters of acid added to that point are used to calculate solution alkalinity similar to that of a Gran titration method. The reader is referred to section 6.6 of the NFM (Appendix C-1) for further discussion of procedures to follow in the field measurement of alkalinity.

Waters of **higher alkalinity** or buffering capacity due to an abundance of carbonate, bicarbonate, hydroxyl or other species that act as a base, tend to be **less susceptible to effects of acid deposition, acid mine drainage, or other anthropogenic acid inputs**. Thus the measurement of alkalinity/ANC is important in **determining the susceptibility of a particular water body to acid input threats**. In general, water bodies in carbonate terrain have elevated alkalinities and good buffering capacity and are less susceptible to acid inputs whereas, for example, water bodies such as high mountain lakes in igneous rock (e.g. granite) terrain, commonly have low alkalinity and little acid

buffering capacity. These latter surface waters are most susceptible to acid atmospheric deposition.

#### 5.2.4.3.2 Calibration, Measurement, Units, and Reporting

Alkalinity is determined with wet chemical methods (titration) in both the field and lab and no field probe has been developed for its direct measurement. However, calibration of the pH meter used in the titration should be performed according to the manufacturer's specifications prior to the alkalinity/ANC determination. Difficulties encountered in the alkalinity measurement are similar to those in the pH measurement (low ionic strength water etc.). State and other Federal agency protocols to follow for the determination of field alkalinity, may or may not be similar to those specified in the NFM (1998) for NAWQA. Care should be taken by Network staff to note any differences between State protocols being considered and the NAWQA program protocols recommended here as the former may need to be adopted. Recommended calibration and standardization procedures are outlined in section 6.6.2 of the NFM (Appendix C-1).

The measurement of alkalinity and ANC and concentration of bicarbonate, carbonate, and hydroxide species are determined using either the inflection point titration (IPT) method or the Gran function plot (Gran) method to analyze the titration data. This requires some familiarity with or understanding of when best to apply these methods. Section 6.6.4 A & B of the NFM (Appendix C-1) provides the details of the alkalinity/ANC analysis including titration procedures, use of the burette and digital titrators, constructing a Gran function plot, and performing the necessary calculations. It is important to have some idea of the likely alkalinity range of the water bodies being measured to facilitate preparation for the alkalinity measurement and method selection. The USGS has developed a **computer software program** to facilitate endpoint determinations of the alkalinity titration in the field.

Alkalinity and ANC should be reported in milliequivalents per liter as  $\text{CaCO}_3$  equivalents for bicarbonate and carbonate, if possible. If reporting in mg/L bicarbonate and carbonate alkalinity, when concentrations are less than 1000 mg/L for either of these species one should use whole numbers; when concentrations are greater than 1000 mg/L, rounding to three significant figures is recommended. Conversion factors are provided in Section 6.6.6 of the NFM. It may also be measured in milliequivalents/liter (meq/L)  $\text{HCO}_3^-$  and converted to the appropriate unit for reporting purposes. Other field methods (HACH) of determining alkalinity may be acceptable to regulatory agencies or alkalinity may be determined through laboratory analysis if data objectives are met.

#### 5.2.4.4 Secchi Disc Transparency (Secchi depth)

Measurement of Secchi disc transparency has historically been the most common

means of measuring water clarity due to its simplicity. It is a qualitative evaluation of the transparency of water to light based on the reflection of light from the surface of the Secchi disc (usually 20 cm in diameter) and is a function of the absorption characteristics both of the water and its dissolved and particulate matter. The secchi disc transparency is the **mean depth of a point where a weighted white disc disappears when viewed from the shaded side of a vessel and that point where it reappears upon raising it after it has been lowered beyond visibility** (Wetzel, 1983). An example of Secchi disc transparency measurement procedures (dos and don'ts under a variety of conditions etc.) are presented at <http://www.tnrcc.state.tx.us/admin/topdoc/gi/252/swqmpdoc.pdf>.

### 5.3 Geomorphic (Stream Morphology) Monitoring Parameters

Geomorphic monitoring documents changes in the existing physical character of stream channels by accurately making and replicating stream channel measurements over a period of years. Geomorphic observations are a smaller subset of overall habitat observations (see Part B, and EPA 1999. **Aquatic Habitat Indicators and their Application to Water Quality Objectives within the Clean Water Act, EPA 910-R-99-014**, available at:

[http://yosemite.epa.gov/R10/ecocomm.nsf/6da048b9966d22518825662d00729a35/f25bad58f59599058825679a005c6983/\\$FILE/Ahi\\_fina.pdf](http://yosemite.epa.gov/R10/ecocomm.nsf/6da048b9966d22518825662d00729a35/f25bad58f59599058825679a005c6983/$FILE/Ahi_fina.pdf) ).

With respect to the more limited topic of stream morphology parameters and stream flow dynamics, some of the more important geomorphic monitoring parameters are used to document the natural rhythm of a stream (e.g. seasonal rise and fall of water, lateral migration of channels across a floodplain etc.). These include a monumented cross-section, a longitudinal profile, a pebble count, and a discharge measurement. Over time and once a baseline is established for these parameters, this information may be used to 1) monitor trends in fluvial and geomorphic conditions, 2) quantify environmental impact, 3) assess stream and watershed response to management, 4) provide channel and flow data for water allocation and supplement other databases, 5) support resource inventories, and 6) track cumulative effects for drainage areas.

Geomorphic monitoring can often complement water quality data in assessing impacts to a stream system and separating responses of a natural system to natural conditions or events from those caused by man. A practical and concise guidance published by the USDA entitled "Stream Channel Reference Sites: An Illustrated Guide to Field Techniques; by Harrelson et. al. (1994) addresses the main elements (above) of geomorphic monitoring and should be useful to Networks developing protocols. This guide covers the minimum needed to accurately characterize stream channels and provides a technically correct way to make the measurements. These include procedures (w/examples) for selecting a site, mapping the site location, measuring the channel cross-section, surveying a longitudinal profile of the channel, measuring stream flow and bed material, and documenting the information in permanent files.

## 5.4 Network Selected Water Quality Measurements

Networks will determine all water quality parameters to be measured that supplement the four (4) required water column parameters of temperature, specific conductance, pH and dissolved oxygen and whether quantitative or qualitative flow/level data will be collected. These few “core” parameters were identified as those parameters that could be measured relatively inexpensively to meet minimum Servicewide goals for evaluating data consistency, completeness, and comparability across all Networks. This limited required parameter list also allows Networks to retain as much flexibility as possible in addressing local monitoring needs cost effectively. It is anticipated that each Network’s Science Advisory committee (or water quality technical subcommittee/workgroup) will identify through the Planning and Assessment process the principal environmental impacts or “stressors” to the significant water bodies of the Network. With this information, the appropriate indicator parameter(s) or best surrogate parameter(s) will be chosen during design of the monitoring program to monitor effects of that stressor on water quality as well as those parameters necessary to meet regulatory requirements under the Clean Water Act (for more details, see Part A and Part B of this guidance).

Supplemental parameters for measurement may be selected on either a site-specific basis or on a Network-wide basis, depending on whether an impact to water quality by a particular stressor is local or is of more regional impact and recurs at multiple Parks. Who will conduct the monitoring, where to monitor, what measurement parameters to include at each monitoring station, their frequency of measurement, how best to conduct the monitoring (partnering), and cost to acquire various parameters will be important considerations by Network personnel in the design of the overall monitoring network. This process will likely require multiple iterations to achieve an effective monitoring system given the cost constraints and complexities of working cooperatively or partnering with one or more other monitoring organizations.

From WRD’s perspective, the tenets of the previous general monitoring guidance provided by the I & M Program in the “Briefing Materials for the Vital Signs Monitoring Meeting” bare reemphasizing for water quality monitoring as well. They are:

- 1) **Monitoring a few things well is better than monitoring several things poorly (i.e. emphasize data quality over data quantity).**

This would apply to both numbers of monitoring stations (sites) and numbers of parameters to monitor for. Begin with a conceptual design of the monitoring program at the Network level and view it in the context of a long-term program that follows an evolutionary process, particularly in the first few years or shakedown/pilot period. In subsequent years, the program will likely expand (add monitoring stations and parameters) as expertise and experience is gained, additional resources are applied, and sampling methodologies are perfected or streamlined through the exchange of information across Networks and with other agencies.

**2) Time is well spent in establishing a very detailed and exacting monitoring protocol at the start to meet the primary goal of water quality monitoring (i.e. to scientifically detect and document change over the long term in 303d listed waters, ONRWs, and water bodies identified as a significant resource to NPS).**

Monitoring protocols must be developed locally due to varying regulatory requirements of States and the cooperative relationships that may form with other agencies. However, standards should be sufficiently high that the resulting data will have Servicewide integrity and application so as to meet NPS objectives for use of the data. Although some modification to protocols will likely be necessary as part of a learning curve, it is best if these protocol changes occur early on in the program and are of minor significance, thus maintaining comparability with previous collected data. Therefore, strive to get it as right as possible the first time by testing and evaluating the effectiveness of the procedures up front and/or early on in the program. Be assured, it will require more resources than you think to collect meaningful and representative data that will meet data quality objectives (e.g. long term trend analysis and differentiating anthropogenic effects in the context of natural variability).

**3) Quality Assurance (the programmatic/institutional measures taken to ensure quality) and Quality Control (sampling methodologies and protocols employed to ensure quality) are key components of the program and are necessary to ensure credibility of and confidence in data, for the program to survive personnel turnovers, and to allow Servicewide or other agency data comparisons (see Part B for more detail).**

In addition to QA/QC, some level of manpower should be appropriated for review and analysis of the tabulated data to catch any obvious measurement or transcription errors. Budgeting for some statistical support or expertise in analyzing the data is also recommended.

**4) Adequate staffing, training, and necessary support facilities and equipment devoted solely to water quality monitoring is a must for those Networks considering in-house implementation of water quality monitoring under the Vital Signs program.**

WRD anticipates that at a minimum, one full time (permanent) water quality technician at the Network level will be required for each Network to support water quality monitoring, if a substantial portion of the monitoring is done in-house. Furthermore, some minimum level of lab facilities at a Park centrally located to the Network monitoring stations, will be needed to support field parameter measurements (calibration and testing of field instruments) and sample collection for analysis by off site laboratories. Some staff training will be necessary until an adequate level of experience in water quality monitoring is acquired. For example, the state of Wyoming has implemented a five-phase training program covering 17 days of instruction for its Conservation District employees to ensure the collection of “credible data”. Credible data laws are also being enacted by states in various areas of environmental monitoring.



In many instances, Networks may elect to develop increased levels of expertise and training of in-house personnel through working jointly with cooperators/partners such as the USGS or States during the initial years of program development.

### 5.5 Monitoring and Sampling Frequencies

Answering certain questions requires that sampling intervals be as short as possible to maximize the utility and representativeness of the data. After years of collecting water quality data, some State and Federal regulatory agencies are **moving towards monthly sampling** in many of their longer term monitoring programs and to meet TMDL requirements. In some cases, weekly, bi-weekly or monthly sampling frequencies are most typical, while in other situations, sites may not be accessible at all times of year. Sampling locations and frequencies are mostly driven by the questions to be answered (see Part B, Section V. A. of guidance). Overall statistical study design considerations (Part B, Section V. B.) should be consulted when thinking through how samples should be distributed in time and space to answer the specific questions discussed in Part B of this guidance at <http://science.nature.nps.gov/im/monitor/protocols/wqPartB.doc> ).

If States or other agencies are being considered for partnering, Networks should consider what sampling frequency (and other) requirements States might have in order to share monitoring costs and build this into the overall Network monitoring program design. Determining sampling frequencies for each monitoring station will be the decision of individual Networks and their cooperators, should be part of the overall monitoring program design, and will be a significant cost consideration.

In general, when appropriate to answer specified questions and not impractical due to seasonal inaccessibility, WRD also recommends that **monthly sampling** be considered by Networks. Also as previously indicated, WRD suggests that each Network consider deployment of a continuous monitoring system for the core parameters (and possible others) when needed to answer specific questions or **to obtain some baseline characterization of variability** (daily, monthly, seasonal) at their key water bodies in the Network. This would provide insight into what additional water quality information is made apparent by sampling at shorter measurement intervals or may be missed entirely by grab sampling between extreme weather events (e.g. first flush effects on chemical load). Rotational deployments of continuous monitors at key waterbodies/representative waterbody types across a Network may also be a means of establishing and archiving variability in key water resources early in the program for later reference.

### 5.6 Associated Field Measurements and Metadata

It is very important to have **complete “metadata” recorded** and readily accessible for all sites and parameters. Metadata typically includes: time of day, the weather conditions, and other environmental conditions under which samples were collected; sample handling, storage, preparation and preservation; sample type (filtered,

unfiltered) and the types of analyses conducted; specific methods of analysis; and the QA/QC measures that were taken. Metadata and associated reporting for field measurements significantly overlaps that metadata required for STORET. The reader is referred to Part B and Part E of this Guidance for further discussion of metadata needs related to data management using STORET and to the discussion below on data required to complete field forms. Examples of various field forms used by NAWQA and others are also provided in Appendices C-1, C-2, C-3, and C-4. Examples of calibration forms, worksheets, and some calibration tips are found in Appendix C-5.

## 5.7 Field Forms

Field forms are completed by the sampling team to **document the manual collection of measurements and associated metadata**. Collection of metadata is done at the site at the time the data is collected to ensure that no critical information or metadata is omitted during data acquisition. Completed field forms provide important sources of information that can **permit some reconstruction of field activities, aid in resolution of some subsequent problem that may be found in the data, and assist in some assessment of QA/QC of the overall data set, troubleshooting, and checking of results**. In addition to the documentation contained in an **instrument logbook**, typical field forms include a **calibration worksheet** for documenting activities that may have occurred associated with calibration of a particular sensor (e.g. membrane change for a DO sensor, wiper change for a turbidity probe, cleaning of the electrodes of a conductivity cell etc.). Some multiparameter instrument vendors supply a recommended calibration worksheet that query's the technician on the critical information to document in the field to achieve the most representative results possible. An example calibration worksheet from YSI and "calibration tips" for making water quality measurements in the continuous monitoring (unattended) mode is also provided in Appendix C-5.

For data comparability purposes, it is often helpful to use field forms identical to or very similar to field forms used by the monitoring group having the most regional and comparable data. These may be State agencies, the USGS, or other groups. EPA is also a source of "standard" forms. For example, **EPA recommends field forms for habitat and biological observations at rivers and streams at** (<http://www.epa.gov/owow/monitoring/rbp/>).

## 6.0 References and Other Information Sources

### 6.1 References Cited

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**6.2 Internet Sites List (w/ brief explanation); The sites thought to be the most useful are highlighted in bold.**

1. **The primary water quality monitoring protocol for sample collection and processing by the USGS is found at:**  
<http://water.usgs.gov/owq/Field Manual/>
2. **USGS guideline for deployment of continuous monitors is found at:**  
<http://water.usgs.gov/pubs/wri/wri004252/>
3. **NAWQA protocols (a.) and an excellent example of State (TX) protocols (b.) more directly driven by the CWA are found respectively at:**
  - (a.) <http://water.usgs.gov/nawqa/protocols/doclist.html>
  - (b.) <http://tnrec.state.tx.us/admin/topdoc/gi/252/swqmproc.pdf>
4. **NAWQA QC Design for surface water sampling is found at:**  
<http://water.usgs.gov/nawqa/protocols/OFR97-223/ofr97-223.pdf>
5. **State-by-state look at Clean Water Act regulations (NPDES, TMDL, Biological Monitoring, Numeric and Narrative Criteria etc.) with POC lists is found at:**  
[http://www.rivernetwork.org/cleanwater/cwa\\_search.asp](http://www.rivernetwork.org/cleanwater/cwa_search.asp)
6. **USGS water analysis methods for toxics (with links/various methods) is found at:**  
<http://toxics.usgs.gov/toxics/measurements.html>
7. **EPA (a.) bio-monitoring protocols and (b.) bio-criteria guidance are found at:**
  - (a.) <http://www.epa.gov/owow/monitroing/rbp/ch04main.htm>
  - (b.) <http://www.epa.gov/ost/biocriteria/stressorI.D.>
8. **A sea water equation of state calculator (salinity)**  
<http://ioc.unesco.org/oceanteacher/resourcekit/M3/Converters/SeaWaterEquationOfState/Sea%20Water%20Equation%20of%20State%20Calculator.htm>
9. **EPA lab accreditation listing under new NELAC program is found at:**  
<http://www.epa.gov/ttn/nelac/accreditlabs.html>

**10. EPA organic and inorganic analysis guidance w/ CERCLA and CLP defaults:**

<http://www.epa.gov/r10earth/offices/oea/r0qadrg.htm>

**11. EPA guidance on volunteer monitoring and QAPP guidance is found at:**

<http://www.epa.gov/owow/monitoring/vol.html>

<http://www.epa.gov/owow/monitoring/volunteer/qappcorr.html>

**12. EPA watershed alliance is found at:**

<http://www.epa.gov.owow/watershed/wacademy/wam/>

(or as zipfile – use above + wamguide.zip)

**13. National Water Quality Monitoring Council is found at:**

<http://wi.water.usgs.gov/pmethods/elements/elements.html>

**14. Water Quality monitoring program in British Columbia (automated sampling):**

<http://www.gov.bc.ca> (multiple sites incld. pubs, aquatics, hydro, design)

/ric/pubs/aquatic/

“ hydro/assets/hydro.pdf

“ design/Design3.htm

“ ambient

“ /Ambient-06.htm#6.4

**15. Information on Pesticides found at:**

<http://ace.ace.orst.edu/info/extonet/> (Extension Toxicology Network)

<http://www.speclab.com/compound/chemabc.htm> (chem. fact sheets)

<http://www.chemfinder.com> (chemical finder)

<http://www.ace.orst.edu/info/nptn/> (national pesticide telecom. Network)

**16. Information on Nutrients found at:**

<http://www.epa.gov/OST/Rules/index.htm/#open>

**Brief Vendors List** (listing here does not imply NPS endorsement of products)

[www.YSI.com](http://www.YSI.com) (manufactures water quality monitoring sondes/probes)

[www.hydrolab.com](http://www.hydrolab.com) “ “

[www.In-Situ.com](http://www.In-Situ.com) “ “

[www.Horiba.com](http://www.Horiba.com) “ “

[www.stevenswater.com](http://www.stevenswater.com) “ “

<http://dbcp.nos.noaa.gov/dbcp/1/obm.html> (list of buoy vendors)

[www.Campbellsci.com](http://www.Campbellsci.com) (manufacturers data loggers/sensors)

[www.HACH.com](http://www.HACH.com) (manufactures probes and field water analysis kits)

### 6.3 Other Available Information (prototype Network documents)

1. Northern Colorado Plateau Network – Planning and Assessment Phase **Scope of Work** for Cooperative (CSU)
2. Northern Colorado Plateau Network – **Water Quality Monitoring Questionnaire** sent to Network's Parks
3. Northern Colorado Plateau Network **Task Agreement** w/USGS describing work needed to develop a water quality monitoring plan

Interregional or International Water Quality Monitoring Organizations:

1. Global Environmental Monitoring System (GEMS) (UN Envir. Prog.) found at: [www.cciw.ca/gems](http://www.cciw.ca/gems)
2. Great Lakes Environmental Monitoring Program found at: [www.glc.org/waterquantity/wrmdss/](http://www.glc.org/waterquantity/wrmdss/).
3. Chesapeake Bay Observing System found at: [www.ceob.nos.noaa.gov](http://www.ceob.nos.noaa.gov)

## 7.0 APPENDICES

### 7.1 Appendix C-1 National Field Manual for the Collection of Water-Quality Data (Book 9)

Download off web at: <http://water.usgs.owo/FieldManual/>

### 7.2 Appendix C-2 Field Guide for Collecting and Processing Stream-Water Samples for the National Water-Quality Assessment Program

Download off web at: <http://water.wr.usgs.gov/pnsp/pest.rep/sw-t.html>

### 7.3 Appendix C-3 Guidelines and Standard Procedures for Continuous Water-Quality Monitors: Site Selection, Field Operation, Calibration, Record Computation, and Reporting

Download off web at: <http://pubs.water.usgs.gov/wri004252>

**7.4 Appendix C-4 State-by-State Look at Clean Water Act with Guidance, Protocols and Multiple Sources of Water Quality Monitoring Information**

Download your state-specific CWA and contact information at:

[http://www.rivernetwork.org/cleanwater/cwa\\_search.asp](http://www.rivernetwork.org/cleanwater/cwa_search.asp)

**7.5 Appendix C-4 Example Field Forms, Calibration Forms/Worksheets and Instrument/Vendor-Specific Calibration Tips**  
See also <http://tnrcc.state.tx.us/admin/topdoc/gi252/swqmproc.pdf> )

**7.6 Appendix C-6 Steps in the Design of a Water-Quality (Monitoring) Information System (reproduced with permission of Dr. Robert Ward) <http://science.nature.nps.gov/im/monitor/docs/ward.doc>**